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THE INVESTIGATION OF THE PREPARATION OF ACRYLON RUBBER MODIFICATIONS UTILIZING COPOLYMER AND TERPOLYMER SYSTEMS

B. DAVID HALPERN

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MONOMER-POLYMER

THE BORDEN COMPANY — CHEMICAL DIVISION

JUNE 1956

WRIGHT AIR DEVELOPMENT CENTER

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WRIGHT AIR DEVELOPMENT CENTER
AIR RESEARCH AND DEVELOPMENT COMMAND
UNITED STATES AIR FORCE
WRIGHT-PATTERSON AIR FORCE BASE, OHIO

FOREWORD

This report was prepared by Monomer-Polymer, The Borden Company - Chemical Division, under USAF Contract No. AF 33(616)-2461. This contract was initiated under Project No. 7340, "Rubber, Plastic and Composite Materials," Task No. 73404, "Synthesis and Evaluation of New Polymers," and was administered under the direction of the Materials Laboratory, Directorate of Research, Wright Air Development Center, with Mr. F. W. Knobloch acting as project engineer.

This report covers work done in the period from May 1, 1954 to May 1, 1955.

Personnel assigned to this project consisted of Drs. B. David Halpern and Wolf Karo. Technical assistance was rendered by Dr. Philip Chen, and Messrs. Benson Chertock and George Crockford.
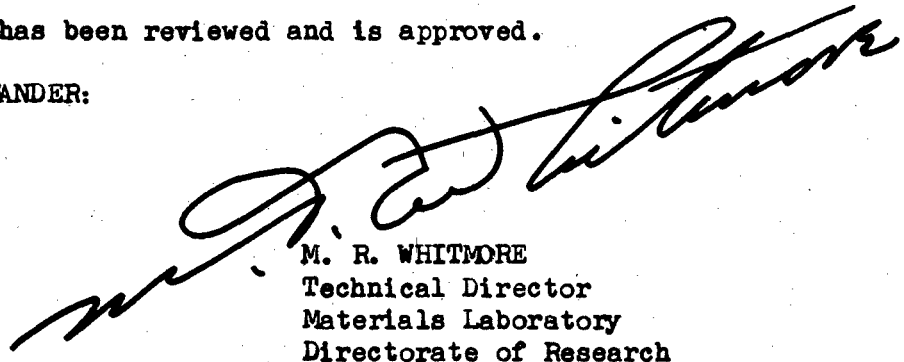
ABSTRACT

In order to improve acrylate-acrylonitrile rubber formulations which exhibit good heat stability and fuel resistance, modifications of this system were investigated using trifluoroethyl acrylate as the major component. Copolymerization of acrylamides with trifluoroethyl acrylate gave elastomers with a number of favorable properties but with high brittle points. Attempts to improve the brittle points resulted in polymers with lower heat stability and higher volume swell. A study of trifluoroethyl acrylate-acrylonitrile copolymers was also made.

PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDER:

M. R. WHITMORE
Technical Director
Materials Laboratory
Directorate of Research

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LEGEND OF ABBREVIATIONS USED

AA	Acrylamide
BA	n-Butyl Acrylate
AN	Acrylonitrile
BAA	N-n-Butylacrylamide
iBAA	N-iso-Butylacrylamide
tBAA	N-tert.-Butylacrylamide
DEAA	N,N-Diethylacrylamide
DMAA	N,N-Dimethylacrylamide
DIOF	Di-iso-octyl Fumarate
DIOM	Di-iso-octyl Maleate
DOF	Di-(2-Ethylhexyl) Fumarate
DOM	Di-(2-Ethylhexyl) Maleate
EA	Ethyl Acrylate
FBA	1,1-Dihydroperfluorobutyl Acrylate
FBAA	N-1,1-Dihydroperfluorobutylacrylamide
MAA	N-Methylacrylamide
MEA	2-Methoxyethyl Acrylate
MAn	Maleic Anhydride
OA	n-Octyl Acrylate
tOAA	tert.-Octylacrylamide
iPAA	N-iso-Propylacrylamide
TFEA	Trifluoroethyl Acrylate
TFEAA	N-Trifluoroethylacrylamide
VC2	Vinylidene Chloride

DISCUSSION

I.   General

The preparation of a number of new monomeric materials and a study of modified acrylon rubber systems were begun under Contract AF 33(616)-252.

It had been found that the basic Acrylon rubber formulations exhibited good heat stability and good fuel resistance when cured. The results of this earlier research suggested that polymers having either ethyl acrylate or butyl acrylate as major components would show an improvement in heat stability and fuel resistance, if the minor constituent of the copolymer systems consisted of vinyl butyrate, acrylamide, or a monomer containing an ether linkage. Copolymers of trifluoroethyl acrylate with acrylonitrile had also shown promise.

In the present contract, a closer integration of the two-fold program — monomer synthesis and polymer preparation – was envisioned.

As projected early in the program, the emphasis was to be on polymerization studies involving Acrylon rubber modifications. The synthetic phase of the program was to consist mainly of the preparation of compounds directly required for the polymerization work or specifically requested for the complementary program at Wright Air Development Center.

Trifluoroethyl acrylate was chosen as the major component for most modified Acrylon copolymers, since previous experience with it had been promising.

The tentative research program of this project initially called for trifluoroethyl acrylate (TFEA) to be copolymerized with various acrylamides and with acrylonitrile at several concentrations. For the purpose of rapid screening procedures, it was found convenient to evaluate the raw polymers. Uncompounded and uncured Acrylon rubber samples prepared analogously to experimental polymers, were used as standards in the study. It was generally reasoned that new formulations which showed improvement over the Acrylon rubbers (uncured) would also show similar improvements in vulcanized stocks. It was hoped that the following problems would receive some elucidation, particularly with respect to N-alkylacrylamide comonomers:

a)   The effect of an increased proportion of the minor comonomer constituent;

b)   The effect of an increased molecular weight of the monomer as a homologous series is used as the minor constituent and the related effects which may arise as a result of an odd or even number of carbon atoms being present in a molecule;

c)   The effect of chain branching or of isomerism;

d)   The effect of substituting acrylamides for acrylonitriles;

e)   The effect of substituting trifluoroethyl acrylates for ethyl acrylate in Acrylon rubber copolymers.

It was assumed that the polymers that have been prepared in this program were linear in character and that they would have approximately the same molecular weight distributions. Otherwise comparisons with respect to these five points might not be valid.

Suspension polymerizations were used when applicable because of their general convenience and control. However, this method was believed to be severely limited, since water-soluble monomers (like acrylamide) might not copolymerize readily in an aqueous dispersion. In such cases, actual analysis of the copolymerization products indicated that appreciable quantities of nitrogen were present, but the existence of a true copolymer was not definitely established. At best, only a fraction of the total of a water-soluble component was present in the final polymeric product.

The copolymers of trifluoroethyl acrylate and amides were generally found to have a number of favorable physical properties. However, the brittle points of these elastomers were rather high. Several copolymerizations were, therefore, carried out with a random selection of monomers as minor components in the hope that polymer chains formed with these radically different constituents would have greater flexibility at low temperatures. The improvements attained in lowering the brittle point were not significant and always were gained at the expense of properties such as volume swell and heat stability.

II.   Monomer Preparation

A.   Trifluoroethyl Acrylate

Considerable quantities of TFEA were consumed in this project, since it was the major component of virtually all of our copolymers.

Initial preparation of TFEA was by treatment of trifluoroethanol with freshly distilled acrylyl chloride in ether solution in the presence of triethylamine. The product used for polymer preparations had a boiling range of 91-92.5°C/749 mm.. In the course of the product distillation, substantial quantities of high boiling materials of unknown composition were isolated.

Subsequent preparations made use of inhibited acrylyl chloride. In these cases, the yield dropped appreciably although some unreacted trifluoroethanol could usually be recovered. A total of five preparations was carried out.

B.   Acrylamide and N-Alkylacrylamides

By treating the appropriate amines in benzene solution with distilled acrylyl chloride, monomers like N-methylacrylamide, N-n-butylacrylamide, and N,N-dimethylacrylamide were prepared. In working up some of these reaction mixtures, care had to be taken that no water washes were used since some of the products seemed to be surprisingly water-soluble.

A few other acrylamides were available in limited quantities. Those monomers that were liquids were purified by distillation just prior to use, the solids by crystallization.

The substituted acrylamides freshly prepared for the work were:

> N-methylacrylamide
> N-iso-propylacrylamide
> N-n-butylacrylamide
> N-iso-butylacrylamide
> N-tert.-butylacrylamide
> N,N-diethylacrylamide
> N-1,1-dihydroheptafluorobutylacrylamide

N-trifluoroethylacrylamide
N,N-dimethylacrylamide

To prepare such comonomers as N-1,1-dihydroperfluorobutylacrylamide by the generalized reaction scheme:

$$C_3F_7CO_2Me + RNH_2 \longrightarrow C_3F_7CONHR \longrightarrow C_3F_7CH_2NHR$$

$$C_3F_7CH_2NHR + CH_2 = CHCOCl \longrightarrow C_3F_7CH_2NRCOCH = CH_2,$$
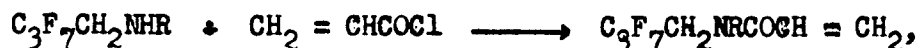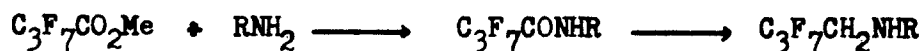
methyl perfluorobutyrate was prepared in 83% yield.

The reduction with lithium aluminum hydride to 1,1-dihydroperfluoro-butylamine was quite trouble-free. It was noted that, when a solution of per-fluorobutyramide in ether was added to a cold solution of lithium aluminum hydride, only very slight refluxing took place. Our previous experience with this sort of reaction had indicated that the reduction is a slow one - contrary to the intuitive assumptions about the use of $LiAlH_4$. Indeed, if we allowed for a prolonged period of contact of the reagent solutions, the yield could be stepped up considerably.

With acrylyl chloride in the presence of triethylamine and of barium chloride, this amine reacted to product N-1,1-dihydroheptafluorobutylacrylamide in 89% yield.

The preparation of N-1,1-dihydrotrifluoroethylacrylamide was carried out twice. The first preparation was particularly effective. Perfluoroaceta-mide was reduced with lithium aluminum hydride by allowing the reactants, after mixing at ice temperature, to be stirred together at room temperature for approximately three days. The reaction was then treated in turn with ethyl acetate and with water. The reaction mixture was distilled and all distillates collected up to 65°C (b.p. of 1,1-dihydrotrifluoroethylamine: 37°C) were preserved over potassium hydroxide.

After adding triethylamine, an inhibitor, and barium chloride to the dried distillate, acrylyl chloride was added. The yield of N-1,1-dihydrotri-fluoroethylacrylamide, based on perfluoroacetamide, was 39.3%. This repre-sented a substantial improvement over the 8.4% previously reported (1).

In the second run, the quantities of reactants were chosen so that at the completion of the reaction a relatively slight excess of lithium aluminum hydride would remain. It must be pointed out though, that these conditions have been used before with other compounds. After approximately sixty percent of the amide solution had been added, the reaction was interrupted over night. Addition was continued the next morning. As usual, the additions were carried out at the temperature of an ice-salt bath. Then the mixture was allowed to warm to room temperature.

The addition of perfluoroacetamide to the reducing agent had been completed for some time and it was thought that raising the temperature of the reaction system cautiously could effectively be substituted for the prolonged treatment at room temperature. Such treatment we believed to be perfectly safe in view of our experience with various related reductions. Gradually warm water was added to the ice bath. The temperature of the bath remained at about ambient conditions for several hours. Suddenly a formation of light-colored platelets was noted in the reacting solution. Similar observations had not been made by us neither in the previous preparation nor in related syntheses.

Along with these platelets, a sludge tended to form on the bottom of the flask which interfered with the proper operation of the stirrer. It was noted that when this sludge was agitated slightly, vigorous bubbling took place. Suddenly a violent explosion occurred. It is possible that an attempt to re-start the stirrer at some point during the reaction was the immediate cause of same.

A review of standard preparative methods for amines in such books as those by Sidgwick (2) and Wagner and Zook (3) did not yield any suitable alternate procedures for the preparation of N-fluoroalkyl substituted acrylamide.

The reduction of amides seems to be confined to the use of lithium aluminum hydride, electrolytic methods, or the use of hydrogen at 200-300 atmospheres, 250-265°C, and copper chromite in dioxane solution (4,5,6). The use of lithium aluminum hydride for use with fluorinated amides was suspended in this Laboratory, however.

The reduction of nitro compounds (7) or oximes might be possible, if these could be obtained. Perhaps an extension of the method of Cook, Pierce, and McBee (8) may afford a few partially fluorinated aminoalcohols having two non-fluorinated carbon atoms immediately attached to the amino group.

The reduction of nitriles with sodium and butanol was considered a possible solution to the problem until it was found that the first member of the series, perfluorobutyronitrile, boils at $5^{\circ}C$, a temperature at which this reduction would probably be very difficult to carry out (9). Reductions involving sodium and alcohols are usually carried out by adding a solution of alcohol and oxidizing agent to metallic sodium at the reflux temperature. With one of the reaction components boiling below room temperature, this would imply the use of some special equipment, such as an autoclave with special provision for adding sodium to the fluid charge after the apparatus had been sealed.

It should be pointed out that these procedures would lead to primary amines only. Further N-alkyl substitutions would involve the usual difficulties encountered in preparing secondary from primary amines.

III.   Partially Fluorinated Monomers Containing Ether Linkage

The determination of the properties of the copolymer TFEA-5AN by personnel of the Materials Laboratory indicated that such properties as fuel resistance, hardness, elongation, modulus, tensile strength, etc. were quite satisfactory. However, a serious shortcoming of this copolymer was its relatively high brittle point. This difficulty was also anticipated for all the fluorinated acrylate esters - acrylamide copolymers.

The possibility of lowering the brittle point by the introduction of an ether linkage was considered. It was thought that this effect would be particularly noticeable when the oxygen replaces a difluoromethylene group since it would bring about chain lengthening with considerable saving in molecular weight, since the number of highly electron attracting fluorine atoms should be reduced somewhat, and since, from the steric point of view, rotations involving $-- CF_2 -- O -- CH_2 --$ seemed easier than rotations involving

$$-- CF_2 -- \underset{\underset{F}{|}}{\overset{\overset{F}{|}}{C}} -- CH_2 \ .$$
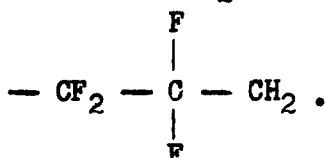
Since the concern was with obtaining acrylate types, we were interested in first obtaining an ether of the general structure $A - O - B - OH$, where either B or preferably A would be a fluorocarbon residue. The preparation of such unsymmetrical ethers seems to be pretty well confined to the methods of Williamson and of Ullman.

In the former case, sodium alcoholates are treated with alkyl halides to form the ether (10)(11):

$$RX + NaOR' \longrightarrow NaX + ROR'$$

The Ullman method utilizes the reaction of alkyl halides with an alcoholate in the presence of copper-bronze powder (12). This method seems to be particularly applicable to the phenolic series. By the utilization of an excess of a glycol and carefully calculated amounts of sodium and alkyl halides, it is possible to prepare monoethers of glycols.

A novel variation of these procedures is that of Hughes, Ingold, and co-workers (13) which involves the interaction of alkyl halides with alcohols in

the presence of silver oxide catalized with a silver salt. In this case the active reagent is the adsorbed silver ion which is maintained at an essentially constant concentration by the silver oxide. The silver oxide is also said to furnish an active surface for the reaction.

A.   2-Perfluoropropoxyethyl Acrylate

Since 2-hydroxyethyl acrylate was available to us, attempts were made to convert the free hydroxyl group to the perfluorinated ether.

1-Iodoperfluoropropane was purified by distillation and diluted with benzene to a known concentration. It was necessary to follow this procedure, since the iodide has a high vapor pressure at room temperature and manipulation of the pure compound was somewhat difficult.

Treatment of 2-hydroxyethyl acrylate with an equivalent amount of 1-iodoperfluoropropane solution in benzene with a mixture of silver oxide and silver nitrate at room temperature and at reflux brought about no chemical change.

When a solution of 2-hydroxyethyl acrylate and 1-iodoperfluoropropane in benzene was treated with sodium metal, nothing but a tar-like polymer was isolated after the metal had been deactivated with alcohol and the solvents had been removed by distillation. From the method of isolation that was used in this reaction, it is entirely possible that this polymer was simple 2-hydroxy-ethyl polyacrylate.

Since these reactions were unsuccessful, it was decided to prepare 2-perfluoropropoxy-1-ethanol and then to convert the ether-alcohol to the acrylate. The anticipated reactions were:

$$CF_3CF_2CF_2I + HO-CH_2CH_2ONa \longrightarrow NaI + CF_3CF_2CF_2OCH_2CH_2OH$$

$$C_3F_7OCH_2CH_2OH + ClCOCH = CH_2 \longrightarrow C_3F_7OCH_2CH_2OCOCH = CH_2$$
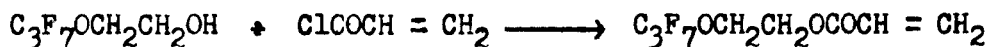
The required amount of sodium was added to a large excess of ethylene glycol. A solution of 1-iodoperfluoropropane in benzene was added. After reflux the low boilers were distilled out. A substantial fraction was

collected between 55° and 70°C. This may have been perfluorohexane (b.p. 57° at 760 mm., (14)). If this is so, a new type of reaction would seem to have been observed here.

Although this synthesis of C_6F_{14} would resemble the Wurz reaction superficially, it will be recalled that the classical procedure involves the treatment of alkyl halides with sodium in an inert solvent such as ether or benzene. Our reaction, however, was carried out with sodium glycolate in ethylene glycol, a highly polar solvent.

The fact that these reactions of 1-iodoperfluoropropane did not proceed as anticipated may involve some considerations such as these: The iodine in this compound may be split off as a positive iodine ion because of the strong electron attracting effect of the fluorine groups (15). Thus a fluorocarbon residue with a negative charge, a fluorocarbon ion, would be left. The glycolate ion is also negatively charged. The interaction between two negative ions is highly improbable. The mechanism for the formation of perfluorohexane, if indeed it had formed, is obscure. The fate of the iodine also would require further elucidation.

B.   1-Iodoperfluoropropane

Our supply of 1-iodoperfluoropropane had been depleted in these earlier experiments. To prepare a new quantity of the material, it was decided to attempt the development of a convenient method of preparation. The basic procedure of Hauptschein and Grosse (16),

$$CF_3CF_2CF_2CO_2Ag + I_2 \longrightarrow AgI + CF_3CF_2CF_2I + CO_2$$
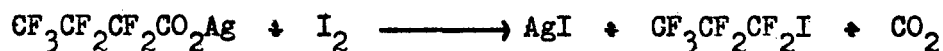
is carried out by heating and stirring the dry reactants. This has proved to be inconvenient. On the one hand the iodine sublimes out readily at the temperature of the reaction. The product, however, is said to inhibit further decomposition. Hence, the product has to be swept out of the reaction flask from time to time, while it is hoped that not too much iodine will be lost.

The obvious modification under these circumstances was simply one of attempting to pass iodine vapors over or through a bed of silver perfluorobutyrate.

In one experiment, iodine was sublimed into the top of a vertical heated glass column filled with a dispersion of silver perfluorobutyrate and coarse, activated alumina. Although there seemed to be some evidence of reaction, it was found too difficult to pass iodine vapor downward through this column.

In a second experiment, the iodine was distilled up through the heated column. This appeared to be somewhat easier than the attempt to go in the reverse direction. However, despite heating the column with iodine for several days, only one or two drops of a liquid product were noted, although the yield should have been on the order of 30 grams. The column, at the end of this time contained a light yellow powder dispersed throughout the alumina. This may well have been silver iodide.

The remote possibility existed that 1-iodopropane had been adsorbed on the alumina. Therefore water was passed through the column packing. However, aside from a small quantity of iodine, nothing resembling a dense, water insoluble liquid halogen compound was observed.

C.   1-(1,1-Dihydroperfluorobutoxy)-3,3,3-trifluoro-2-propyl Acrylate

Part of our synthetic program was devoted to the preparation of the intermediates required for a number of other monomers containing ether linkages.

The proposed reactions were:

$$CF_3COCH_3 + Br_2 \longrightarrow CF_3COCH_2Br + HBr$$

$$(I)$$

$$CF_3COCH_2Br + R_fCH_2OH \longrightarrow CF_3COCH_2OCH_2R_f$$

$$(II)$$

where $R_f = CF_3$ or C_3F_7

$$CF_3COCH_2OCH_2R_f \longrightarrow CF_3CH(OH)CH_2OCH_2R_f.$$

$$(III)$$
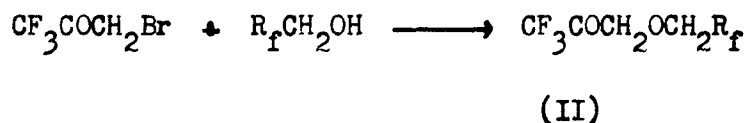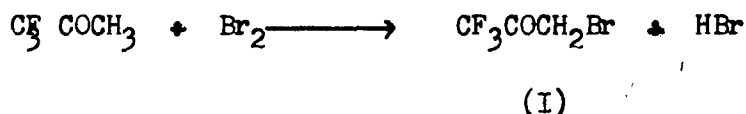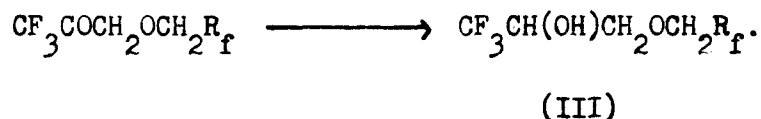
The compound (III) was to be converted to the acrylate to give monomers

of the structure

$$R_fCH_2OCH_2 - \overset{\overset{\displaystyle CF_3}{|}}{CH} - O - \overset{\overset{\displaystyle O}{\|}}{C} - \underset{\underset{\displaystyle R}{|}}{C} = CH_2$$
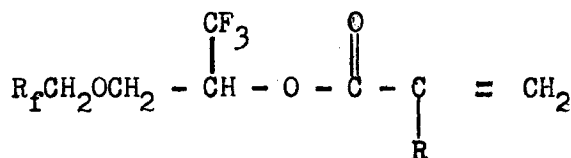
(IV)   Where R = H or CH_3

Compound (III) may also be dehydrated to the monomer $CF_3CH = CH_2OCH_2R_f$.

Compound (II) may be reduced with $LiAlH_4$ and through subsequent reactions give rise to various new types of monomers:

$$CF_3COCH_2Br \longrightarrow CF_3CH(OH)CH_2Br .$$
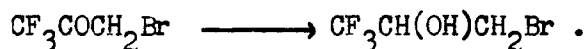
(I)   (V)

Compound (V), with acrylyl chloride or methacrylyl chloride may be converted to

$$BrCH_2 - \overset{\overset{\displaystyle CF_3}{|}}{CH} - O\overset{\overset{\displaystyle O}{\|}}{C} - \underset{\underset{\displaystyle R}{|}}{C} = CH_2$$
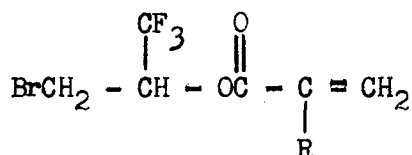
(VI)

Conversion of (V) to the oxide may lead to the following reaction sequences:

$$CF_3\underset{\underset{\displaystyle OH}{|}}{CH} - \underset{\underset{\displaystyle Br}{|}}{CH_2} \longrightarrow CF_3 - \overset{\diagdown}{CH} - \overset{\diagup}{CH_2}$$
$$O$$

(V)   (VI)

$$CF_3CH - CH_2 + R_fCH_2OH \longrightarrow CF_3CH(OH)CH_2OCH_2R_f \quad (III)$$

$$\underset{O}{\diagdown\diagup}$$

(VI)

and

$$R_fCH_2O \overset{\overset{\displaystyle CF_3}{|}}{CH} - CH_2OH \;.$$

(VII)
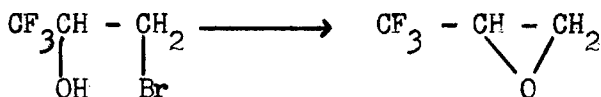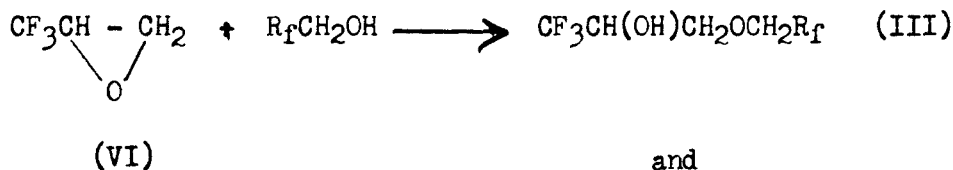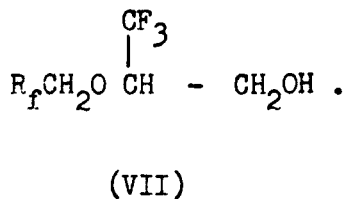
Compound (VII) may be converted to the acrylate, the methacrylate, or dehydrated to the vinyl type monomer

$$R_fCH_2O \overset{\overset{\displaystyle CF_3}{|}}{C} = CH_2.$$
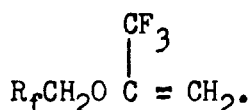
The current synthetic work was directed toward a compound of type (IV),

$$CF_3CF_2CF_2CH_2OCH_2 - \underset{\underset{\displaystyle CF_3}{|}}{CH} - O - \overset{\overset{\displaystyle O}{\|}}{C} - CH = CH_2 \;.$$

(IV a)
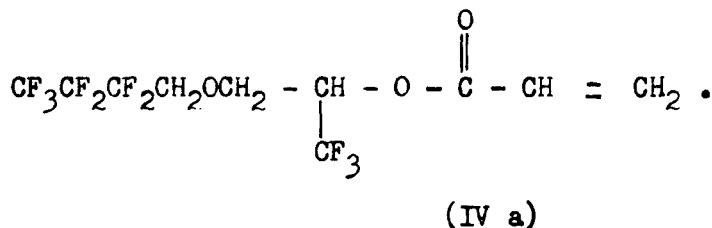
The bromination of trifluoroacetone by the method of McBee and Burton (17) proceeded smoothly in a yield of 73%. Reaction of 3-bromo-1,1,1-trifluoropropanone with aqueous sodium 1,1-dihydroperfluorobutoxide gave a surprisingly low weight of water insoluble product. The boiling range of this product was from 83 to 91°C (b.p. of 1,1-dihydroperfluorobutanol: 95°/749.7 mm. (18)).

To obtain more material for careful rectification, a larger run was carried out. In this second run, one equivalent of sodium hydroxide pellets was kept in contact with two equivalents of 1,1-dihydroperfluoro-1-butanol overnight to form the sodium salt. The resulting mixture was fairly rigid; however on addition of the bromo compound, the character of the mixture changed and before long clearly resembled a suspension of a salt in a fluid. The early stages of the addition of the bromotrifluoropropanone were carried out at slightly elevated temperatures. At that time, the reaction was exothermic in

nature. When external heating was discontinued, the reaction appeared to be substantially slower.

Two substantial fractions were fractionally distilled from the reaction mixture:

	B.P.	n_D^{20}
A.	89-93°C	1.3320
B.	93.5-98°C	1.3133

To remove only the butanol, which might be present and which might prevent clear-cut separation of product, those fractions were recombined and thoroughly washed with sodium hydroxide solution. The other extracts of the aqueous solution and the water insoluble layers were combined, dried, and fractionally distilled. The fractions isolated were:

	B.P.	n_D^{20}	% C found	% H found
A-2	93-96°C	1.3130	31.4	3.06
B-2	97°C	1.3319	29.9	2.65

The alkaline solution from the wash was added to concentrated sulfuric acid and distilled. A substantial quantity of material boiling at 100°C was collected - at best, an aqueous solution of organic product, C-2, which was isolated. The refractive index of this material $n_D^{27.5}$ was 1.3396.

Neither fraction A-2 nor B-2 formed hydrazones or 2,4-dinitrophenyl-hydrazones. Both seemed to react with metallic sodium. Preliminary experiments designed to identify these compounds indicated that benzoates may be formed on reaction with benzoyl chloride. The N-alpha-naphthylurethane of A-2 had a melting point (uncorrected) of 79-80°, of B-2, 79.5-81°. The melting point of N-alpha-naphthyl-1,1-dihydroperfluorobutylurethane is reported as 77 to 78° (19). Infrared spectra of A-2 and B-2 showed that these two fractions were, a) identical and b) alcohols with no keto group present. Whether an ether link was present or not could not be ascertained.* The conclusion is, therefore, that the alkali wash had not been sufficiently extensive to dissolve all of the 1,1-dihydroperfluorobutanol that had been present in the reaction system. The fate of the 3-bromo-1,1,1-trifluoropropanone could not be ascertained because the contract time was running out. Either the desired product

* We should like to express our gratitude to Dr. S. Batacharya, Harvard University, for the infrared spectral analyses.

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or a derivative of the starting bromo-ketone may have been present in the product C-2.

IV.   Studies With Polymers

   A.   Suspension Polymerizations

      In the course of this investigation, a large group of copolymers was prepared. The favored methods used were variations utilizing dispersions of polymerizing monomers in water. In a few cases, however, bulk polymerizations were used.

      In Table I, the compositions of several copolymers are given. In this table, the "nominal" percentage of the minor constituent of the copolymer is derived simply from the original composition of the monomer mixture that had been polymerized. The "found" percentage of the minor constituent is based on an actual micro-Dumas nitrogen analysis of the product. The discrepancies between these two values are considered not at all unusual in the suspension copolymerization field. Many reasons may be advanced of contributing factors such as water solubility of the monomers, inadequate purification of the product because of their low solubility in conventional solvents, incomplete reaction of one of the monomers and subsequent removal of it by steam distillation.

TABLE I

Composition of Some Rubbers

(Suspension Polymerization)

Major Component	Minor Component	Nominal Wt. % of Minor Component	Found Wt. % of Minor Component	% Yield of Polymer
EA	AA	5	1	88.4
"	tBAA	5	—*	90.6
"	"	5	—*	86.2
"	"	5	8.2	88.5
"	"	12	13.6	87.8
TFEA	tBAA	1	trace	84.8
"	tBAA	5	5.5	88.8
"	AN	1	1.2	92.5
"	AN	5	3	78.8
"	AN	10	6	70.0
"	iBAA	5	5.5	92.7
"	iBAA	10	11	90.8
"	MAA	5	trace	84.4
"	MAA	10	1.8	68.8
"	BAA	10	10	91.8
"	BAA	5	4.5	90.2
"	iPAA	5	5.6	80.4
"	iPAA	10	9.6	80.8
"	DEAA	5	10	37.8
"	DEAA	10	21	36.0

* Not submitted for analysis.

Earlier experiments involving ethyl acrylate had been carried out to gain experience in suspension polymerization techniques while using water soluble comonomers.

The difficulties arising from the water solubility of the monomers is pointed out in Table I for the polymerization of EA with AA, where only one percent unit of a possible five percent of AA was found in the final product.

Variation in polymer yields was mainly attributed to losses of the portion of polymer which was in emulsion form rather than in the form of beads at the end of the process.

The possible explanations for the increase in percentage of nitrogen-containing-component may be related to the difficulties found in the purification of these polymers. During the preparations, bits of glass and of compounded rubber may have gotten into the reaction vessels. It was found that the newly made materials were very insoluble in many common solvents.

Trifluoroethyl polyacrylate was formed when a bottle of uninhibited trifluoroethyl acrylate polymerized while in storage. The resulting polymer was a clear, rubbery material. It is referred to throughout this report as TFEA (bulk).

In a series of polymer preparations, the percent composition of comonomer solution has been given in terms of mole percent. We adopted this practice because it would seem that a much fairer comparison of properties of copolymers having different minor components can be made, if the number of molecules available for inclusion in each polymer is essentially the same. For example, a copolymer of TFEA with 5 weight percent of FBA contains 0.02 moles of the latter material in every 100 g. of comonomer solution, while a copolymer of TFEA with 5 weight percent of acrylonitrile contains 0.1 moles of acrylonitrile in every 100 g. of comonomer solution.

By similar reasoning, it may be shown that for copolymers of the same pair of monomers, a difference of a factor of 2 in mole percent units in the minor constituent, will usually represent a much more radical change in composition than a factor of 2 in weight percent units. Therefore, the extreme effects of such concentration changes are more readily demonstrated.

The technique used in these preparations was essentially the same as that used earlier. The only modifications used were:

1. The substrate consisted of 200 ml. of distilled water containing 3 ml. of a 1% solution of Polyco 270 A.

2. The total weight of monomeric solution used was 25 grams.

3. The weight of freshly precipitated dibenzoyl peroxide was 0.025 grams.

A suspension polymer of TFEA by itself was also prepared TFEA-(pearl).

A suspension copolymerization of FBA-39.6 mole % of AN (equivalent to FBA-12 wt. % AN) was carried out in order to check the effect of substituting 1,1-dihydroheptafluorobutyl acrylate for trifluoroethyl acrylate.* The polymerization proceeded quite slowly and the conversion was low. The final copolymer seems to soften considerably about 100°C.

Even softer was the copolymer of FBA-20.2 mole % AN. At the moment, these materials are believed to be mechanically unsuitable as high temperature elastomers. This may be the result of a rather low average molecular weight. Hence direct comparison with the analogous trifluoroethyl acrylate copolymer may not be strictly valid.

The possibility of reducing the brittle point by admixture of such a FBA copolymer to a TFEA copolymer or incorporation of FBA in a terpolymer system involving TFEA was considered.

Samples of TFEA-10 mole % FBA and TFEA-50 mole % FBA were prepared. Our technique for preparing these and many subsequent copolymer samples involved shaking a mixture of the monomers, catalyst, water, and dispersing agent in a capped soft-drink bottle in an oven maintained at the appropriate temperature. In many cases this gave quite satisfactory yields of "pearl" polymers.

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* The fluorinated ester had been made available to us through the courtesy of the Minnesota Mining and Manufacturing Company, for which we should like to express our gratitude.

This technique was of particular value in the preparation of copolymers that involved a highly volatile monomer. Thus TFEA-10 mole % VC2 and TFEA-25 mole % VC2 were conveniently prepared. These products were found to have a rather crystalline character. The copolymer of TFEA and 25 mole % VC2 seemed to have a resin-like consistency. It could be readily molded under moderate pressure and temperatures to give a tough, flexible, transparent, slightly rubbery sheet with an elongation greater than 380% and a tensile greater than 635 psi.

Two copolymers that involved maleic anhydride were prepared: TFEA-10 mole % MAn and TFEA-25 mole % MAn. The maleic anhydride was soluble only to the extent of approximately 25 mole percent in TFEA even at $60^{\circ}C$. However, an attempt was made to copolymerize these amounts in any case. It was our intention to utilize the TFEA-MAn system to place various ester links at various points along the copolymer chain by reacting the anhydride functions of the product in the presence of various alcohols. It seemed possible that some control over the crystalline character of the copolymer might be attained by introducing irregularities in the copolymer chain.

The preparation of diverse copolymer systems was attempted with a view to lowering the brittle point of copolymers. The general technique used was very similar to that mentioned above. Since it seemed undesirable to run our reactions with a mechanical shaker operating in an oven at 80°C, we decided to attempt the polymerizations at room temperature by use of a "redox" initiation system. If a filterable product was not obtained after a reasonable time, azobiisobutyronitrile was added as an initiator. In many cases, this also did not form a filterable product. Lauroyl peroxide was then added and polymerization allowed to proceed for a more extended period, often at slightly elevated temperatures. Yields were still not very high, but at least a few copolymers were formed in sufficient quantity to permit further working up.

Such a procedure was adopted because our initial experience with this series of copolymers indicated incomplete reaction even after 15 hours at room temperature with a "redox" initiator. For example, in the preparation of TFEA-5 FBA-5 AN, polymerization seemed to have taken place at room temperature. The product could not be separated by filtering through a fine silk bolting cloth. After centrifuging the fluid, 0.52 g. of polymer was isolated. The theoretical yield was 25 grams. Therefore, in subsequent experiments, the sequence of initiators indicated above was added in an attempt at least to convert a reasonable fraction of the monomers. This procedure, of course, may lead to cross-linked polymers.

Since conversions in these last polymerizations were quite low, many of them had to be repeated several times.

Lauroyl peroxide did not appear to be an effective initiator for the TFEA-DOM and for the TFEA-DOF systems. Therefore hydrogen peroxide and cupric ions were added to these systems and polymerization carried out at slightly higher temperatures.

Five terpolymers, which were slight variations on the TFEA-5AN copolymer system, were prepared in order to study the effect of the third monomeric constituent on the low temperature flexibility. Conversions, by and large, were low.

Table II gives the nominal compositions and yields of the more recently prepared suspension copolymers. Since all of these elastomers contained TFEA as major components, only the concentrations of the minor components are given. For the terpolymers, concentrations are given in terms of weight percent.

In line with a request from WADC, we also prepared approximately 300 g. of TFEA-5AN by the suspension method. Nitrogen analysis of this copolymer showed it to be, in fact, TFEA-4.2 AN.

TABLE II

Composition of Some Rubbers Based on TFEA (I)

(Suspension Polymerization)

(Note: m% = mole percent)

Minor Component A		Minor Component B		Yield, Per Cent
10m%	iBAA			56
5m%	iBAA			42
10m%	TFEAA			88
5m%	TFEAA			74
10m%	FBAA			72
5m%	FBAA			88
— (pearl) —				92
10m%	FBA			82
50m%	FBA			76
10m%	VC2			93
25m%	VC2			90
10m%	MAn			83
25m%	MAn			74
10m%	OA			94
5m%	OA			94
10m%	DIOF**			61
5m%	DIOF			7
10m%	DIOM**			34
5m%	DIOM			23
10m%	DOM**			35
5m%	DOM			71
10m%	DOF**			81
5m%	DOF			77
5	FBA	5	AN	83
5	MEA	5	AN	71
1	MEA	5	AN	29
5	OA	5	AN	90
1	OA	5	AN	45

** We should like to express our gratitude to the Rubber Corporation of America for making samples of these four compounds available to us.

B.   Bulk Polymerization

Table III lists a series of TFEA bulk copolymers which were generally prepared in 20 g. lots. This technique was used to prepare copolymers which contained water soluble monomers and hence could not adequately be prepared by the suspension method.

As in the case of some of the suspension copolymers described above, a few copolymers were prepared in bulk to permit some comparison with similar material made by other methods. Bulk polymerizations were carried out between 74° and 80°C in glass cells prepared from lantern slides, spaced about 3 mm. apart, and held together by an impregnated paper tape. After the reaction had been completed, the separation of the polymer sheet from glass presented a difficult problem. Several parting agents were tried as coatings for the glass cell interior but these were of no avail. Finally the glass was simply removed by cracking it and chipping it off.

The preparation of TFEA-acrylamide copolymers seems to have as an upper limit the approximately 2 mole % AA composition. The acrylamide dissolved in TFEA with difficulty when warmed and crystallizes out readily on cooling.

TABLE III

Compositions of Some Rubbers Based on TFEA (II)

(Bulk Polymerization)

(Note: m% = mole percent)

Minor Compound

	TFEA (Homopolymer)
4.8m%	DMAA
9.5m%	DMAA
4.8m%	DEAA
9 m%	DEAA
10 m%	AN
5 m%	AN

C. Fusion of Copolymers

Samples of some of the uncured and uncompounded copolymers were warmed gradually on a hot plate. The sequence in which the materials fused was noted. In some cases, the elastomer would not fuse down but maintained vestiges of its original gross structure even after considerable resistance to fusion on heating.

It was observed that TFEA-10 iPAA started only to color fully 20 minutes after TFEA-1 tBAA had melted, that it was still "lumpy" 20 minutes after TFEA-5 iBAA had started to melt and that an additional 25 minutes were required before it had fused appreciably. In Table IV, the copolymers which did not fuse down completely are marked with a single asterisk.

Near the softening point, all of the copolymers darkened perceptibly. Trifluoroethyl polyacrylate (bulk) fused to a clear orange fluid with a relatively small degree of discoloration.

It is interesting to observe that stability of at least one set of copolymers (EA - 5 tBAA) seems to be related at least as much to the nature of the aqueous suspending medium used as to the nature of the monomers involved. It appears that with an increase in the starch concentration, the resistance to fusion is increased. However, the time interval between the first two cases was relatively short.

With two exceptions, TFEA - BAA and TFEA - iBAA, an increase in the concentration of the minor component was followed by an increased resistance to the fusing action of heat. TFEA - 5 DEAA and 10 DEAA appeared to fuse simultaneously or nearly so. The TFEA - iPAA copolymers appeared to be outstanding in regard to this test.

TABLE IV

Sequence of Fusion of Several Copolymers

TFEA	–	1	tBAA
TFEA	–	1	AN
	EA –	5	AA
TFEA	–	10	BAA
TFEA (bulk)			
	EA –	5	tBAA**
(TFEA	–	5	DEAA)
(TFEA	–	10	DEAA)
	EA –	5	tBAA**
TFEA	–	10	iBAA*
TFEA	–	5	MAA
TFEA	–	5	BAA
TFEA	–	5	AN
	EA –	5	tBAA**
	EA –	12	tBAA
TFEA	–	5	tBAA
TFEA	–	10	MAA*
(TFEA	–	10	AN
(TFEA	–	5	iBAA*)
TFEA	–	5	iPAA*
TFEA	–	10	iPAA*

* Polymers did not fuse completely

** The only known difference in these three polymers was in the polymerization recipe; the concentration of starch in the aqueous phase was increased as we read down the table.

D.   Heat Resistance of Copolymers

Samples of uncured, uncompounded polymers were heated in open aluminum dishes at constant temperature and the loss in weight determined. For the first two hours, samples were cooled and weighed after heating at 100°C for half hour intervals. This treatment was followed by heating samples at 210°C for 15 hours. The loss of weight after the full period is given in Table V, where the arrangement is in order of increasing weight loss.

TABLE V

Heat Resistance of Several Raw Copolymers at Moderately High Temperatures

Copolymer Composition			% Weight Loss 2 hours @ 100°C 15 hours @ 210°C
TFEA	5	iPAA	0.91
TFEA	5	tBAA	1.49
TFEA	10	iPAA	1.90
TFEA	5	AN	2.26
TFEA	10	DEAA	2.73
TFEA	10	BAA	2.82
TFEA	5	iBAA	2.96
EA	12	tBAA	3.18
TFEA	10	AN	3.30
EA	5	tBAA	3.34
TFEA	10	iBAA	3.47
TFEA	5	DEAA	4.45
EA	5	AA	4.77
TFEA	10	MAA	5.38
TFEA	5	MAA	5.80
TFEA	5	BAA	6.40
TFEA	1	AN	6.48
TFEA	(bulk)		8.53
TFEA	1	tBAA	9.16

A plot of percent weight loss with time at 100°C for a few of these polymers showed that all samples lost some weight during the first half hour. In the second half hour, each showed some increase in weight over its previous weight, and in some cases even over its initial weight. The behavior of the samples after the first hour was variable, but there seemed a general trend toward a loss in weight. No explanation for these observations is offered.

Similar experiments were carried out with six uncured elastomers that had been milled with 35 parts Philblack O to each 100 parts of raw polymer.*

Table VI lists the percent total weight loss of polymers containing carbon black at various times at $96° \pm 3°C$. The behavior was again found to be erratic, however, not as extreme as in previous cases.

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* We should like to express our gratitude to the staff of WADC for their cooperation and effort in connection with the milling operations.

TABLE VI

Data of Weight Loss vs. Time at $96° \pm 3°C$

Composition	Initial Wt. of sample,g.	15 min.	30 min.	45 min.	Total % Wt. Loss After:					
					1 hr.	1.5 hrs.	2 hrs.	2.5 hrs.	3 hrs.	4 hrs.
EA - 12tBAA	0.7773	0.45	0.61	0.57	0.55	0.68	0.52	0.73	0.76	0.70
TFEA- 1tBAA	0.6057	.38	.35	.35	.33	.33	.35	.48	.36	.48
TFEA- 10AN	0.7577	.36	.41	.40	.36	.56	.53	.54	.44	.53
TFEA- 10iBAA	0.7090	.25	.47	.41	.40	.43	.40	.43	.48	.55
TFEA- 5MAA	0.9512	.23	.31	.31	.27	.35	.40	.35	.48	.48
TFEA- 10iPAA	0.5835	.53	.58	.19	.36	.36	.41	.41	.41	.41

In another heat test, samples milled with carbon black were exposed for 72 hours at $148° \pm 5°$ C. The % weight loss is presented in Table VII. Simultaneously, six raw rubbers were also tested. The data for these are given in Table VIII. It is interesting to note that whereas differences between the items of Table VII* are small, the variation from data in Table VII to corresponding data in Table VIII is generally quite large. A possible explanation that may be offered is that the increased heat stability of the copolymers may be mainly the result of the presence of the carbon-black filler.

TABLE VII

Heat Resistance Test — Milled Rubbers

(72 hours at $148° \pm 5°C$)

Polymer Composition		Total % Wt. Lost	Polymer Composition		Total % Wt. Lost
TFEA	— 5m% FBAA	0.21	TFEA	— 5AN	.86
TFEA	— 5iPAA	.68	TFEA	— 10iPAA	.86
EA	— 5AA	.69	TFEA	(pearls)	.92
TFEA	— 5BAA	.70	TFEA	— 5m% iBAA	.94
EA	— 5tBAA	.70	TFEA	— 5m% TFEAA	.96
TFEA	— 10m% FBAA	.76	TFEA	— 1tBAA	.97
TFEA	— 10BAA	.77	TFEA	— 5MAA	1.04
TFEA	— 10iBAA	.77	TFEA	— 10AN	1.14
EA	— 12tBAA	.78	TFEA	(bulk)	1.23
TFEA	— 1AN	.83	TFEA	— 5tBAA	1.24
TFEA	— 10m% TFEAA	.85			

Median: 0.85%
Average: 0.86%

TABLE VIII

Heat Resistance Test — Raw Rubbers

(72 hours at $148° \pm 5°C$)

Polymer Composition		Total % Wt. Lost
TFEA	— 5iPAA	0.72
TFEA	— 5AN	5.2
TFEA	— 5m% FBAA	7.0
TFEA	— 5m% TFEAA	9.3
TFEA	— 10m% FBAA	9.5
TFEA	— 1tBAA	13.4

Median: 8.15%
Average: 7.52%

The variation in weight loss from sample to sample for the milled elastomers is not very great. The average weight loss (arithmetic mean) is 0.85%, based on 21 milled samples; the standard deviation is 0.217, which represented a coefficient of variation of 25.5%

Assuming a continuous distribution, and that the weight losses are essentially random variations, it will be noted that the weight loss of the TFEA - 5m% FBAA copolymer was substantially less than average (0.21% compared to 0.85%). Since 99.7% of all possible cases are to be found within ± 3 standard deviation units of the arithmetic mean, it would appear that this case just falls at the limit, and may be regarded as a possible unique case. Computing arithmetic means etc. without the value for TFEA - 5m% FBAA milled copolymer, we obtain an arithmetic mean for the remaining 20 samples of 0.89%, a standard deviation of 0.17, and a coefficient of variation of 19.2%. Thus we appeared to have evidence that one of our new copolymers had significantly better resistance to the action of dry heat.

In an effort to differentiate more conclusively between the qualities of these elastomers, 21 of the milled but uncured elastomers and the 6 raw elastomers which had already been subjected to the heat treatment reported upon above were returned to the oven and heated for an additional 90 hours at 204° ± 5°C. Table IX lists the total % weight loss at 148° and 204° ± 5°C after a total of 162 hours in order of increasing loss of weight for the milled rubbers. Table X lists the same information for the raw rubber.

TABLE IX

Heat Resistance Test   -   Milled Rubbers

(72 hours at 148° ± 5°C followed by 90 hours at 204° ± 5°C)

Polymer Composition	Total % Wt. Lost	Polymer Composition	Total % Wt. Lost
EA - 12tBAA	4.9		
EA - 5AA	5.1	TFEA - 1AN	10.6
EA - 5tBAA	5.3	TFEA - 5m% TFEAA	10.6
		TFEA - 5MAA	10.7
TFEA - 5m% iBAA	8.9	TFEA - 1tBAA	11.2
TFEA - 5BAA	9.0		
TFEA - 5iPAA	9.2	TFEA - 10m% FBAA	12.1
TFEA - 5AN	9.4	TFEA - 10iBAA	12.9
TFEA - 5m% FBAA	9.5	TFEA - 5tBAA	13.6
		TFEA (pearls)	13.8
TFEA - 10m% TFEAA	10.0	TFEA - 10AN	14.4
TFEA - 10iPAA	10.1		
TFEA - 10BAA	10.2	TFEA (bulk)	16.3
	Median: 10.2%		
	Average: 10.4%		

TABLE X

Heat Resistance Test — Raw Rubbers

(72 hours at 148° ± 5°C followed by 90 hours at 204° ± 5°C)

Polymer Composition	Total % Wt. Lost
TFEA — 5iPAA	5.5
TFEA — 5AN	20.9
TFEA — 5m% FBAA	31.6
TFEA — 5m% TFEAA	33.8
TFEA — 1tBAA	36.6
TFEA — 10m% FBAA	39.8

Median: 32.7%
Average: 28.0%

The standard deviation for the data of the milled elastomer is 2.88, which represents a coefficient of variation of 27.7%.

The spread of values had actually decreased by prolonging the heat and time factor (4.9 to 16.3%, a 3.3 fold range, as compared to 0.21 to 1.24%, a 5.9 fold range for the case of more moderate heat treatment). Yet the coefficient of variation had increased, probably indicating more the influence of the extreme values rather than the higher degree of differentiation. If we ignore the 3 EA — based copolymers and the bulk polymer of TFEA, the mean for the data becomes 11.0%, the standard deviation 1.71, and the coefficient of variation is then 15.5%, which seems to indicate a somewhat closer grouping of the data about the mean value. The values dropped for this calculation are also found to be outside the 3 standard deviation units limit and must probably be considered to have a different heat stability than the majority of the samples.

It may be purely fortuitous that the sequence of increasing weight loss for the raw elastomers (Table X) is the same as that of the milled rubbers (Table IX), although this is to be expected.

The most striking observation to be made from these data is that the three ethyl acrylate copolymers withstood the heat treatment better, at least from the point of view of weight loss, than the trifluoroethyl acrylate copolymers.

This may possibly be attributed to the fact that trifluoroethyl polyacrylates have trifluoroethyl branches on the main chain which split off at some critical temperature. The result may not necessarily imply scission of the backbone chain of the copolymer. The removal of such groups as CF_3CH_2-,

CF_3CH_2O -, or $CF_3CH_2O\overset{\overset{O}{\|}}{C}$ - may perhaps be facilitated by the strong electronic influence of the fluorine atoms on molecular fragments of these dimensions.

The copolymer of TFEA and 5m% iBAA appears to be the best of the TFEA copolymers. It should be noted however that 5m% of iBAA represents 4.3 weight percent. The difference in properties between a copolymer with 4.3% iBAA and one containing 5% iBAA is rather large. In our statistical discussion, above, we assumed that this is a random variation in measuring essentially the same value. If this is so, more precise methods of measuring weight loss are required.

If these data are assumed to be fairly precise, the sequence from 4.3% iBAA, to 5% iBAA, 10% iBAA indicates a maximum weight loss in the 5 to 10% range, close to the 5% region. Since pure TFEA (pearls) has as little heat resistance as the 5% iBAA copolymer, the assumption of fair precision in these experiments would tend to lead to an irregular shaped composition vs. % weight loss graph. It must be emphasized, however, that these data leave out of consideration effects of different molecular weight distributions, cross-linking, etc.

Another method of evaluating the data is based on the assumption that the volatile fragments generated are the original monomers, and that these monomers leave the bulk of the polymer in the exact ratio in which they were mixed for polymerization. It is then possible to assign a "pseudo-molecular weight" to the material lost on heating the polymer.

We assign a "pseudomolecular weight" (PMW) to the monomer mixture thus:

Let a be the weight of component A in 100 g. of the comonomer solution, and let 100-a be the weight of component B in 100 g. of the comonomer solution.

Let M_A be the molecular weight of component A, and M_B be the molecular weight of component B.

Then $\dfrac{a}{M_A}$ and $\dfrac{100-a}{M_B}$ are the number of moles of A and B respectively in 100g. of comonomer.

The pseudomolecular weight of the mixture is then computed from the relationship:

$$\frac{a}{M_A} + \frac{100-a}{M_B} = \frac{100}{PMW}$$

If the fractional weight losses (computed from Table IX) are divided by the corresponding PMW's, a weight loss term is obtained which we call the "Molar" Weight Loss in Table XI. It represents the number of moles of comonomers lost per gram of copolymer.

From this point of view, the range from least to most heat resistant is approximately 2 fold, whereas on the basis of weight loss alone, the range is 3 fold.

The arithmetic mean for the "molar" weight loss data is 0.068%/mole, the median is 0.068%/mole, the standard deviation is 0.028%/mole, and the coefficient of variation is 41%.

By and large the sequence of the copolymers based on molar weight loss parallels the ordinary weight loss data, with a few modifications.

TABLE XI

Heat Resistance Test — Milled Rubbers

On Molar Basis

Polymer Composition		Pseudo-Molecular Weight	"Molar" Weight Loss, 10^2 x %/mole
EA	– 12tBAA	103	4.8
EA	– 5AA	98	5.2
EA	– 5tBAA	100	5.3
TFEA	– 5m% iBAA	153	5.8
TFEA	– 5BAA	153	5.9
TFEA	– 5iPAA	153	5.9
TFEA	– 5m% FBAA	158	6.0
TFEA	– 5AN	141	6.7
TFEA	– 10BAA	151	6.8
TFEA	– 5m% TFEAA	154	6.9
TFEA	– 10iPAA	145	7.0
TFEA	– 1AN	151	7.1
TFEA	– 1tBAA	153	7.3
TFEA	– 10m% FBAA	164	7.4
TFEA	– 10m% TFEAA	154	7.5
TFEA	– 5MAA	147	7.5
TFEA	– 5iBAA	153	8.9
TFEA	(pearl)	154	9.0
TFEA	– 10iBAA	151	9.0
TFEA	(bulk)	154	10.6
TFEA	– 10AN	130	11.1

Median: 0.068%/mole
Average: 0.068%/mole

The molar weight losses, grouped as indicated in Table XI appear to follow the normal Gaussian distribution curve fairly closely. It is an interesting question in statistics, whether one may deduce from this that all the data obtained in this series of experiments are essentially identical with the arithmetic mean while the deviations are the result of random scattering.

The weight loss data for 37 milled copolymers are given in Tables XII and XIII. These tables include previously discussed information as well as that for a number of copolymers that had been prepared toward the end of the contract period. Table XII indicates the percent weight loss after 72 hours at $148^\circ \pm 5^\circ C$, while Table XIII gives the data resulting from treatment of the same polymers at $204^\circ \pm 5^\circ C$ for an additional 90 hour period. These heat resistance tests were carried out in two stages because it was hoped that the second heating period would permit better differentiation between the copolymers, since this had clearly not been possible on the basis of the first heat treatment.

TABLE XII

Heat Resistance Test — Milled Rubbers

(72 hours at $148° \pm 5°C$)

Note: * Copolymers contain no TFEA

Composition; TFEA +	% Wt. Loss		Composition; TFEA +	% Wt. Loss
5m% FBAA	0.21		10m% OA	1.01
			5 MAA	1.04
5OA – 5AN	.59			
5m% OA	.59		25m% MAn	1.12
			10AN	1.14
5 iPAA	.68		10m% MAn	1.15
EA – 5AA *	.69		1 OA – 5AN	1.17
5 BAA	.70		50m% FBA	1.18
EA – 5tBAA *	.70			
5MEA – 5AN	.71		(bulk)	1.23
			5tBAA	1.24
10m% FBAA	.76		10m% DOF	1.27
10 iBAA	.77			
10 BAA	.77		10m% FBA	1.32
EA – 12tBAA *	.78			
5 FBA – 5AN	.79		10m% VC2	1.46
10m% DIOF	.81			
1 AN	.83		5m% DOF	5.29
10m% TFEAA	.85		25m% VC2	18.1
5m% DOM	.86			
5 AN	.86			
10 iPAA	.86			
(pearls) •	.92			
5m% iBAA	.94			
5m% TFEAA	.96			
1 tBAA	.97			

Median: 0.92 %
Average: 1.49 %

TABLE XIII

Heat Resistance Test — Milled Rubbers

(72 hrs. at 148° ± 5°C followed by 90 hrs. at 204° ± 5°C)

Note: * Copolymers contain no TFEA

Composition; TFEA ◆	Total % Wt. Loss	Composition; TFEA ◆	Total % Wt. Loss
5 OA – 5 AN	3.8	10m% FBA	13.1
		5 tBAA	13.6
EA – 12tBAA *	4.9	(pearls)	13.8
EA – 5AA *	5.1		
EA – 5tBAA *	5.3	10 AN	14.4
		5m% DOF	14.4
10m% OA	8.5		
5m% iBAA	8.9	5m% OA	15.5
5 BAA	9.0		
5 iPAA	9.2	(bulk)	16.3
5 AN	9.4	10m% MAn	16.4
5m% FBAA	9.5	25m% MAn	16.8
10m% TFEAA	10.0	10m% DIOF	17.6
10 iPAA	10.1		
10 BAA	10.2	5m% DOM	23.8
1 AN	10.6		
5m% TFEAA	10.6	10m% DOF	28.5
5 MAA	10.7		
1 tBAA	11.2	10m% VC2	32.2
5 FBA – 5 AN	11.4		
1 OA – 5 AN	11.5	25m% VC2	39.5
5 MEA – 5 AN	11.7		
10m% FBAA	12.1		
50m% FBA	12.7		
10 iBAA	12.9		

Median: 11.5 %
Average: 13.1 %

Alongside the milled elastomers, several raw rubbers were subjected to the same thermal treatment as the milled samples. The weight losses tended to be somewhat higher. Table XIV gives the results of the 72 hour test at $148^\circ \pm 5^\circ C$ for a number of raw rubbers. Table XV gives related values for raw rubbers that had been subjected to two heating periods, one at $148^\circ \pm 5^\circ C$ for 72 hours, followed by 90 hours at $204^\circ \pm 5^\circ C$.

TABLE XIV

Heat Resistance Test - Raw Rubbers

(72 hours at $148^\circ \pm 5^\circ C$)

Composition; TFEA +	Total % Wt. Loss
5 iPAA	0.72
5 MEA - 5 AN	2.16
5 AN	5.1
5m% FBAA	7.0
5m% TFEAA	9.3
10m% FBAA	9.5
10m% DIOF	11.4
50m% FBA	11.9
1 tBAA	13.4
5m% DOM	13.5
10m% DOM	18.5
10m% DOF	19.2
25m% VC2	20.9

Median: 11.4 %
Average: 11.0 %

TABLE XV

Heat Resistance Test — Raw Rubbers

(72 Hrs. at 148° ± 5°C followed by 90 hrs. at 204° ± 5°C)

Composition; TFEA +	Total % Wt. Loss
5 iPAA	5.5
5 MEA — 5 AN	8.3
10m% DIOF	19.7
5 AN	20.9
5m% DOM	24.6
10m% DOF	29.9
5m% FBAA	31.6
10m% DOM	31.9
50m% FBA	33.0
5m% FEAA	33.8
1 tBAA	36.6
10m% FBAA	39.8
25m% VC2	55.9

Median: 31.6 %
Average: 28.5 %

E.   Thermal Decomposition of TFEA - 5AN

        Fifty grams of TFEA - 5AN (actual composition TFEA - 4.2 AN) was heated strongly and the decomposition products were condensed in appropriate receivers.

        Between $350°$ and $375°C$, the polymer fused and turned dark. During the first six hours only a few grams of condensible material was collected and those in Dry Ice traps. The polymer was heated for 18 additional hours at $400°C$ and 12mm. pressure. Approximately 30 grams of volatile material was collected in all. The volatiles were fractionally distilled. The last fraction was rather difficult to distill and resinified on heating. The distillation proceeded as follows:

Fraction No.	b.p. $°C$/mm.	Wt., g.	n_D^{20}
I	70 - 76/760	8.89	1.3020
II	76/760	5.91	1.3015
III	100 - 110/8	2.00	1.3764
IV	130 - 179/8	1.68	too viscous
V	207 - 225/8	1.32	too viscous

        Exhaustion of contract funds prevented further identification of these fractions. For comparison, the physical constants of some simple, related compounds are:

Name	b.p. $°C$/mm.	
Acrylonitrile	77 - 77.5/760	n_D^{25} 1.3884 - 1.3888
Trifluoroethanol	74/760	n_D^{22} 1.2907
Trifluoroethyl Acrylate	91 - 92.5/749	n_D^{20} 1.3415 - 1.3470
Acrylic Acid	141/760	n_D^{25} 1.4185

F.   Attempts at Molding

A small mold was prepared with which it was hoped to obtain regularly shaped, highly polished milled rubber test samples.

Efforts at molding were made using milled TFEA - 5AN as the charge. Despite variation of the factors of time, temperature, and pressure, we were not successful. In all, 9 unsuccessful attempts were carried out. The difficulty may be associated with the comparatively high heat stability of the sample.

On the other hand, raw elastomers could be compressed into thin sheets on a Carver press. When these sheets were removed from the press, they tended to contract into a wrinkled cup. Some elastomers, particularly TFEA - VC2 copolymers, formed into smooth, transparent sheets without difficulty, but this seemed rather the exception than the rule. For use in rough brittle point determinations, these sheets seemed quite adequate.

The inability to obtain a press-polished rubber sheet of suitable thickness precluded the possibility of obtaining a Shore A durometer hardness under various test conditions.

G.   Brittle Point Determinations

Preliminary work at WADC had indicated that TFEA elastomers containing acrylonitrile or amides had relatively high brittle points. A selection was made of the raw copolymers that had been prepared in the course of this program. All of these were copolymers in the sense used in this report, i. e., the elastomeric products obtained on polymerization of mixtures of two or more monomers. Rough brittle points were determined on sheets prepared from these rubbers in a Carver press at 65°C and 4000 psi by cooling in a bath and flexing them.

The bath used consisted of a large Dewar flask containing ice, hydrated calcium chloride, and water. By the judicious addition of warm water, it was quite possible to control the bath temperature quite well from - 40°C to room temperature and beyond.

In Table XVI, the results of these tests are summarized. These data may be considered consistent within themselves, but whether other laboratories could

reproduce these results is problematical. So called "skin-effects" may cause difficulties if sheets of different thicknesses were to be used, for example.

TABLE XVI

Brittle Point Determinations

Bath Temperatures

Composition; TFEA +	- 10°C	- 20°C	- 23°C	- 27°C	- 30°C	- 35°C	- 40°C
5MEA - 5AN	OK	Stiff					Brittle
5m% DOM	OK	OK	OK	OK	OK	Stiff	Brittle
1 OA - 5AN	OK	Brittle					
10m% OA	OK	Brittle					
10m% DIOF	OK	OK					Brittle
10m% DOF	OK	OK	OK	OK	Brittle		Brittle
5m% OA	OK	Brittle					
5FBA - 5AN	Brittle						
5 OA - 5AN	Brittle						
5m% DOF	OK	Brittle					

H.   Solubility Tests

Attempts to find solvents for some of the initial polymers proved to be a time-consuming operation. After approximately 120 tests, it was decided to divide the available polymers into groups – those that were soluble in dimethylformamide to the extent of at least 0.1 g. of raw polymer in 50 ml. of solvent and those that were not. The latter group consisted of a small number of polymers that seemed to resist the actions of a large number of solvents of diverse chemical nature.

The determination of solubility of any of the polymers was frequently uncertain because of the swelling of the polymer in the liquid. Very often, the swollen polymer mass would have a refractive index very close to that of the surrounding medium. Furthermore, the solvent frequently seemed to break up lumps of polymer into fine rubber beads much like those formed during suspension polymerization procedures. Consequently, swollen polymers were often well camouflaged in the media. This fact was only recognized when, what appeared to be a solution, was filtered and polymeric gels were found to have been collected on the filter paper.

In Table XVII some of the solubility data that have been accumulated is summarized. The abbreviations that have been used are:

For solvents

DMF	---	N,N-dimethylformamide
EDC	---	ethylene dichloride
T-T	---	70% of toluene, 30% of textile spirits
m-X	---	meta Xylene
CF	---	chloroform
AcMe	---	acetone
MeOH	---	methanol
HOAc	---	glacial acetic acid
CT	---	carbon tetrachloride
THF	---	tetrahydrofuran
TEA	---	triethylamine
EC	---	ethylene carbonate (at ca. 40°C)
MEK	---	methyl ethyl ketone
MO	---	mesityl oxide

For the observations

s	---	soluble
x	---	insoluble, or swelled polymer, no significant amount of solute in solution
s-	---	partially soluble
?	---	doubtful

TABLE XVII

Solubility of Some Copolymers—A

Composition	DMF	EDC	T-T	m-X	CF	AcMe	MeOH	HOAc	CT	THF	TEA	EC	MEK	MO
EA-5AA	s-	x							x	s-				
EA-5tBAA	s-	s							x	s-				
EA-12tBAA	s-	x			s-				x	s-				
TFEA-1tBAA	s	x												
TFEA-5tBAA	s	x												
TFEA-1 AN	s	x												
TFEA-5AN	s	x	x											
TFEA-10 AN	s									s				
TFEA-5iBAA	x	x		x	x	x	x	x	x	x	x	x	x	x
TFEA-10iBAA	x	x			x	x	x			x?				
TFEA-5MAA	s	x												
TFEA-10 MAA	s	x												
TFEA-10 BAA	x			x	s-?	x		x	x					
TFEA-5BAA	x			x	x					x				
TFEA-5iPAA	x?	x		x	x	x				s-				
TFEA-10iPAA	x	x		x	x		x		x				x	x
TFEA-5DEAA	s													
TFEA-10DEAA	x	x			s-									
TFEA-(bulk)	s													

The objectives of this series of tests included solution of the polymers, classification of the polymer solutions by filtration and removal of unreacted monomers by reprecipitation.

Upon dilution of filtered dimethylformamide solutions of the polymers with methanol, no visible precipitates formed (although none of the products was soluble in pure methanol). Therefore the precipitation had to be undertaken with distilled water. This procedure, however, may very well prevent the elimination of monomer from polymer. Attempts at steam distillation of the solutions as a means of removing monomer and precipitating the polymer were not satisfactory. The resulting products invariably were off-color whereas the precipitation method invariably led to white products.

Further attempts were made to dissolve some of these polymers so that they might be purified and so that viscosity data might be obtained on solutions of the polymers. The TFEA-5iBAA copolymer was a particularly intractable material. It was found to be insoluble in ethylene dichloride, dimethylformamide, chloroform, methanol, glacial acetic acid, tetrahydrofuran, carbon tetrachloride, methyl ethyl ketone, mesityl oxide, triethylamine, methyl isobutyl ketone, chlorobenzene, triethanolamine, cresol, concentrated sulfuric acid, and benzotrifluoride, although the latter solvent did seem to swell the copolymer somewhat. The copolymer, TFEA-10iPAA, was also found to be insoluble in concentrated sulfuric acid and in benzotrifluoride.

The solubility of several bulk copolymers is given in Table XVIII. The abbreviation BztF in this table refers to benzotrifluoride.

TABLE XVIII

Solubility of Some Copolymers - - B

| Composition; | Solubility in | |
TFEA +	DMF	BztF
9.5m% DMAA (bulk)	—	x
4.75m% DEAA "	s	s
9m% DEAA "	x	x
10m% AN "	s	—
5m% AN "	s	—
10m% iBAA (pearl)	x	—
5m% iBAA "	s—	—
10m% TFEAA "	s	—
5m% TFEAA "	s	—
10m% FBA "	s—	—
5m% FBA "	s—	—

Screening of the solubility of some of our more recent copolymers was carried out by shaking 0.5 g. of copolymer with 25 ml. of dimethylformamide.

The two TFEA-FBA copolymes and the TFEA-10m% VC2 copolymer were swollen by the solvent, whereas the TFEA-25m% VC2, TFEA-10m% MAn, and TFEA-25m% MAn were found to be soluble.

The polymers in solution could not be reprecipitated readily by the addition of methanol or acetone, although water would always accomplish this.

The polymer TFEA-25m% VC2 seemed to be insoluble in tetrahydrofuran and in methyl ethyl ketone. Both TFEA-MAn copolymers were swelled by toluene or benzene.

The TFEA-5AN copolymer batch prepared toward the end of the contract period was swelled somewhat by butyrolactone, and by N-methyl-2-pyrrolidone, and by benzotrifluoride (1 gram of polymer to 9 grams of solvent). By diluting the mixture more, a very viscous 5% solution could be made with N-methyl-2-pyrrolidone. In 5% dilution, even the butyrolactone seemed to dissolve the polymer at least partially. Bis (trifluoromethyl) benzene was not found to be an effective solvent for this copolymer. At best it swelled the TFEA-5AN copolymer somewhat.

I.   Viscosity Determinations

Preliminary viscosity determinations were made with an Ostwald-Fenske viscometer using a solution of 0.010g. of a randomly selected precipitated polymer diluted to 10.0 ml. with distilled dimethylformamide. Only totally soluble copolymers were used in these experiments. The viscosity of pure solvent was also repeatedly taken so that data for solutions and solvent pairs at the same temperature could be used in our calculations. The data are summarized in Table XIX.

TABLE XIX

Preliminary Viscosity Data
For Soluble Copolymers

Composition; TFEA +	Relative Viscosity	Intrinsic Viscosity, Liters per gram
1 tBAA	1.46	4.6
5 tBAA	1.12	1.2
1 AN	1.22	2.2
5 AN	1.27	2.7
10 AN	1.20	2.0
5 MAA	1.19	1.9
10 MAA	1.11	1.1
5 DEAA	1.17	1.7
(bulk)	1.25	2.5

For these preliminary data, it is assumed that the viscosity of a 0.1 g. per 100 ml. solution is sufficiently close to that at infinite dilution to permit comparison of the data.

The estimation of molecular weight of a polymer from the intrinsic viscosity of its solution, requires several constants. Unfortunately, these constants vary quite appreciably with the composition of the polymer. The methods for evaluation of these values are not relatively simple viscosity determinations. For the large variety of copolymers that we have prepared already, it would take us too far afield to attempt molecular weight estimates for each composition. For the present, the intrinsic viscosities of the dilute solutions of the copolymers will have to serve for characterizing the materials.

If, in the light of the foregoing discussion, the intrinsic viscosities given in Table XIX are used with the appropriate constants for poly-methylmethacrylate in benzene solution at $25^\circ C$ (20), the range of molecular weights would be from approximately 2.8×10^6 for TFEA-1 tBAA to 0.7×10^6 for TFEA-10 MAA.

J.   Swell Tests on Raw Copolymers

Samples of thirty five raw copolymers were placed in individual test tubes. For the sake of comparison, samples of commercial Acrylon EA-5 and Acrylon BA-12 (American Monomer Corporation) were also made up. Each of these samples was covered with approximately 15 ml. of 70% isooctane, 30% toluene mixture. After 5 months, the only qualitative conclusion that could definitely be reached was that Acrylon BA-12 swelled quite appreciably, whereas all the other samples except perhaps the Acrylon EA-5, did not seem to swell appreciably.

A more quantitative swell test was run on 10 copolymers prepared late in the program. Data for these tests will be found in Tables XXIV and XXV. This information is also discussed in Section K, immediately following.

K.   Swell Tests on Milled Rubbers

Two series of swell tests were carried out on elastomer samples that had been milled as previously indicated. The first set of experiments was carried out on twenty-one different copolymers. The general procedure utilized follows.

Rectangular sections of these rubbers, approximately 40 x 10 x 1.5mm., were cut out. The volume was determined by water displacement measurements. After being suspended for fourteen days in jars containing 70% isooctane-30% toluene (by volume), the new weights and volumes were determined. It was interesting to note that the weight increases did not parallel the volume increases. The reasons for negative volume increases are not clear. Simple mechanical losses in the course of weighing and handling may be the cause.

Table XX lists the increasing order of volume-swell of the milled un-cured copolymers with their corresponding weight increases. One sample, EA-5tBAA was so soft at the end of the test that it was not possible to hold it on its wire support for weighing. The first column of the table indicates the composition of the copolymer by giving the percent of minor component monomer

that had been added to trifluoroethylacrylate.

TABLE XX

Swell Test Data for TFEA-based Copolymers

In 70% Iso-Octane: 30% Toluene, at $25° \pm 5°$ C for 14 Days

Composition; TFEA ÷	% Volume Increase	% Weight Increase	Fractional Density Increase % Wt./% V.
10m% TFEAA	-12	5.0	-0.42
1 tBAA	- 3.2	7.2	-2.3
10 iBAA	- 1.7	4.5	-2.7
5m% iBAA	2.3	6.9	3.0
(bulk)	2.9	9.7	3.3
10 AN	3.0	6.4	2.1
(pearl)	4.7	17	3.6
5 iPAA	5.3	6.7	1.3
5 MAA	5.6	5.9	1.1
5m% TFEAA	5.9	8.9	1.5
5m% FBAA	11	12	1.1
10 iPAA	13	12	0.92
10 BAA	14	8.2	0.59
10m% FBAA	15	12	0.80
5 BAA	22	13	0.59
5 tBAA *	24	7.9	0.33
1 AN	24	11	0.46
5 AN	24	9.8	0.24

Composition; EA ÷			
5 AA *	35	26	0.74
12 t BAA *	40	19	0.48

* These values are particularly unreliable because of excessive softness of the swelled rubber.

The median for the volume increase is 8.5%, the average volumetric swell is 11.7%.

The median for the weight increase is 9.3%, the average gravimetric swell is 10.5%.

The last column in the table is the ratio of the percent weight increase divided by the percent volume increase. This quantity represents the fractional increase in the density of the sample. Values in this column that are greater than unity seem to indicate that the polymer has imbibed the mixed solvent without appreciable volume increase, i.e., high adsorption of the solvent. Values between zero and unity are to be expected for elastomers that have been swelled. The negative values may result from contraction of the rubber during exposure to the solvent.

The observations made here are only valid, of course, if they are true experimental facts - not the results of experimental errors or of manipulative difficulties. Reporting these data to only two significant figures is believed to be within the limits of reliability for these single runs. Dimensions of the original sample did not permit experiments of greater precision. Little could be learned from the changes of dimensions of the samples. After prolonged immersion, physical distortions of the rectangular pieces of copolymer were too great to permit determination of the volumes by direct measurements.

A second series of swell tests was carried out with the more recently prepared copolymers. Some of the samples were placed in small baskets fashioned out of brass screening before immersion in solvents.

The weight and volume of these baskets were determined to permit the necessary corrections in the numerical values. These small baskets, approximately 3 cm. deep and 1.5 cm. in diameter, were particularly convenient for testing raw copolymers which were still in the bead form. Screening permitted virtually unobstructed contact between sample and solvent, while the danger of losses due to samples becoming detached from the bulk of the material in the course of the test was minimized.

Table XXI lists the volume swells of all milled copolymers considered in this program in order of increasing volume swell. Table XXII lists the milled copolymers in the order of increasing weight increase of copolymer, under similar circumstances. Table XXIII gives the ratio of % weight increase to % volume

increase. Tables XXIV and XXV give volume swell and weight swell data for a few unmilled elastomers.

TABLE XXI

Volume Swell Test — Milled Rubber

Note: * Copolymer contains no TFEA

Composition; TFEA +	% Volume Increase	Composition;; TFEA +	% Volume Increase
10m% TFEAA	-12	50m% FBA	18
1 tBAA	- 3.2		
10 iBAA	- 1.7	5m% OA	22
		5 BAA	22
5m% iBAA	2.3	1 AN	24
(bulk)	2.9	5 AN	24
10 AN	3.0	5 tBAA	24
(pearl)	4.7	10m% FBA	29
5 iPAA	5.3	25m% VC2	29
1 OA - 5 AN	5.3	10m% OA	29
5 MAA	5.6		
5m% TFEAA	5.9	10m% DICF	33
		EA - 5 AA *	35
5m% FBAA	11	5m% DOF	35
5 MEA-5 AN	12		
10 iPAA	13	EA - 12 tBAA *	40
10m% MAn	14		
10 BAA	14		
10m% FBAA	15		
5 OA - 5 AN	15		
10m% DOF	15		
10m% VC2	15		
5 FBA - 5 AN	16		
5m% DOM	18		
25m% MAn	18		

Median: 14%
Average: 16%

TABLE XXII

Weight Swell Test - Milled Rubber

Note: * Copolymers contain no TFEA

Composition; TFEA +	% Weight Increase	Composition; TFEA +	% Weight Increase
1 OA – 5 AN	1.5	5 AN	9.8
5m% DOM	3.3	1 AN	11
		10m% FBA	12
5 MEA – 5 AN	4.0	5m% FBAA	12
10 iBAA	4.5	10m% FBAA	12
10m% TFEAA	5.0	5m% OA	12
50m% FBA	5.7	5 BAA	13
10m% DOF	5.8		
5 MAA	5.9	5m% DOF	14
5 FBA – 5 AN	6.2	25m% VC2	15
10m% MAn	6.4		
10 AN	6.4	(pearls)	17
10 iPAA	6.7		
5 iPAA	6.7	10m% OA	19
5m% iBAA	6.9	EA – 12 tBAA *	19
1 tBAA	7.2		
10m% VC2	7.7	EA – 5 AA *	26
25m% MAn	7.7		
5 tBAA	7.9		
10 BAA	8.2		
5m% TFEAA	8.9		
5 OA – 5 AN	9.0		
10m% DIOF	9.0		
(bulk)	9.7		

Median: 8.2%
Average: 9.5%

TABLE XXIII

Fractional Density Increase
Milled Rubber

Note: * Copolymers contain no TFEA

Composition; TFEA ♣	Increase % Wt./% Vol.	Composition; TFEA ♣	Increase % Wt./% Vol.
10 iBAA	-2.7	5 BAA	0.59
1 tBAA	-2.3	10m% OA	.63
10m% TFEAA	-0.42		
		EA - 5 AA *	.74
5m% DOM	0.19		
		10m% FBAA	.80
5 AN	.24		
10m% DIOF	.27	10 iPAA	.92
1 OA - 5 AN	.29		
50m% FBA	.32	5 MAA	1.1
5 tBAA	.33	5m% FBAA	1.1
5 MEA - 5 AN	.34	5 iPAA	1.3
10m% DOF	.38	5m% TFEAA	1.5
5 FBA - 5 AN	.38		
5m% DOF	.39	10 AN	2.1
10m% FBA	.40		
		5m% iBAA	3.0
25m% MAn	.45	(bulk)	3.3
1 AN	.46	(pearls)	3.6
10m% MAn	.47		
EA - 12 tBAA *	.48		
10m% VC2	.50		
25m% VC2	.52		
5m% OA	.56		
10 BAA	.59		
5 OA - 5 AN	.59		

Median: 0.47
Average: 0.65

TABLE XXIV

Volume Swell Test - Raw Rubber

Composition; TFEA ♣	% Volume Increase
10m% DOF	11
10m% DOM	12
1 OA - 5 AN	15
5m% DOM	18
5 MEA - 5 AN	18
5 FBA - 5 AN	21
5m% OA	30
5 OA - 5 AN	45
10m% DIOF	86
5m% DOF	100

Median: 19.5%
Average: 35.6%

TABLE XXV

Weight Swell Test - Raw Rubber

Composition; TFEA +	% Volume Increase
5m% DOM	5.6
5 MEA - 5 AN	5.9
10m% DOF	6.4
10m% DOM	7.1
1 OA - 5 AN	7.6
5m% DOF	11
5m% OA	15
5 FBA - 5 AN	15
10m% DIOF	17
5 OA - 5 AN	33

Median: 9.3%
Average: 12.4%

L.   Evaluation of Copolymers

        The purpose of this contract was an attempt to obtain elastomers
with certain specified properties. The data presented in this report may be of
assistance in selecting the direction of further developmental work.

        Low loss of weight on heating, low volume increase and low weight in-
crease on immersion in solvents are desirable. In Table XXVI, in

    Column A, are checked those copolymers that were the nine best at $145^{\circ} \pm 5^{\circ}C$
            for 72 hours (Table XII);

    Column B, those copolymers that were the nine best at both $145^{\circ} \pm 5^{\circ}C$ for
            72 hours and $204^{\circ} \pm 5^{\circ}C$ for an additional 90 hours (Table XXIII);

    Column C, those copolymers that were the nine best (including those with
            negative values) on the volume swell test (Table XXI);

    Column D, those copolymers that were the nine best on the weight swell test
            (Table XXII).

        The number of copolymers selected was 25% of the total tested.

        On the basis of these criteria, TFEA – 5 iPAA has the highest all around
score. Such copolymers as EA – 5 AA, EA – 5 tBAA, and TFEA with minor compo-
nents such as 5 BAA, 5 MEA – 5 AN, 5m% iBAA, 10m% TFEAA, 10 iBAA, and 1 OA–5 AN
may also be considered to have fair properties if the four listed properties
are considered to have equal weight. Of particular interest from the point of
view of high heat resistance and high volume swell resistance would be TFEA –
5 iPAA and TFEA – 5m% iBAA. The two copolymer systems should receive further
attention in future research programs.

TABLE XXVI

Property Rating of Some Copolymers

Composition;

TFEA +	EA +	A	B	C	D
5m% FBAA		x			
5 OA - 5 AN		x			
5m% OA		x			
5 iPAA		x	x	x	
	5 AA	x	x		
5 BAA		x	x		
	5 tBAA	x	x		
5 MEA - 5 AN		x			x
10m% FBAA		x			
5 OA - 5 AN			x		
	12 tBAA		x		
10m% OA			x		
5m% iBAA			x	x	
5 AN			x		
10m% TFEAA				x	x
1 tBAA				x	
10 iBAA				x	x
(bulk)				x	
10 AN				x	
(pearl)				x	
1 OA - 5 AN				x	x
5m% DOM					x
50m% FBA					x
10m% DOF					x
5 MAA					x
5 FBA - 5 AN					x

It had been hoped initially that it would be possible to accumulate enough data in the course of this program to permit correlation of structural features of the monomers with properties.

In Tables XIII, XXI, And XXII the data are grouped. It is assumed, for the sake of this evaluation, that copolymers within each group have property values of identical orders of magnitude, and that copolymers in different groups have distinctly different values of the measured property. In other words, a high degree of accuracy is assumed here, although this is probably not justified. The usual assumption of comparability of materials - freedom from cross linkage and identity of molecular weight distribution - must also be made. It must also be kept in mind that data are used for rubbers that have been milled with carbon black but are uncured.

Even under these circumstances, it is not possible to draw any definite conclusions concerning the effect of increasing the concentration of the minor component in the product. There is a slight indication that increasing the concentration of a non-fluorinated minor component in a TFEA copolymer decreases the heat resistance and resistance of volumetric swell somewhat, while the resistance to weight increases on swelling increases. The observations seem, however, fortuitous.

Equally inconclusive are comparisons of the effect of increasing the length of the alkyl side chain substituted on the nitrogen atom of the acrylamides. Whether the acrylamides are preferable to the acrylonitrile cannot be demonstrated with the data at hand. It does, however, seem that while ethyl acrylate copolymers have better heat resistance than most of those of trifluoroethyl acrylate, from the point of view of resistance to swell, the trifluoroethyl acrylate copolymers are definitely superior.

Thus the data do not permit any definite prediction of the structure desirable in a minor component for copolymerization with TFEA, but they do permit a statement of which one system appears superior to all the compositions studied.

EXPERIMENTAL

I. Monomer Preparation

A. Trifluoroethyl Acrylate

1. In a 5-1. three-neck flask, equipped with a Hirshberg stirrer, addition funnel, and a reflux condenser protected by a calcium chloride tube, was placed a solution of 900 g. (9 moles) of trifluoroethanol and 960 g. (9.5 moles) of triethylamine in 1500 ml. of anhydrous ether.

After this solution had been chilled thoroughly in an ice-salt bath, 840 g. (9.3 moles) of distilled acrylyl chloride was added dropwise over a five hour period.

The reaction mixture was allowed to warm gradually to room temperature and to remain at that temperature overnight. Then the precipitate in the reaction flask was dissolved with a sodium chloride solution. The ether layer was separated. The aqueous phase was extracted with several small portions of ether. The ether solutions were combined and dried over dried magnesium sulfate powder.

The ether was separated by distillation. The product was collected between 91° and 92.5°C/749 mm. Yield: 842.3 g., 61% of theory.

The high boiling residue contained material with b.p. range from 111° to 142°C/749mm., weight 49 g.

A substantial quantity of polymeric residue was also present. This could be removed from the equipment by refluxing with benzene.

2,3. By a similar procedure two preparations afforded 1478 g. of trifluoroethylacrylate in 43 and 62% yields respectively.

4. By treatment of a solution of 600 g. (6 moles) of tri-fluoroethanol, 620 g. (6.2 moles) of triethylamine in 1000 ml. of anhydrous ether, containing 0.1 g. phenothiazine and 0.1 g. of cuprous chloride, with 560 g. (6.1 moles) of acrylyl chloride (inhibited) in 1000 ml. of anhydrous ether, 241.1 g. of trifluoroethylacrylate was isolated, a 26% yield.

5. In a small preparation similar to 4 above, 102.7 g. of product were isolated, which represented a 30% yield.

B. Acrylamides

1. N-Methylacrylamide

To a chilled solution of 122.5 g. (4 + moles) of anhydrous methylamine in 500 ml. of benzene was added a solution of 176 g. (1.94 moles) of distilled acrylyl chloride in 100 ml. of benzene over a 2.75 hour period.

The salts were filtered off. The solvent of the filterate was removed by distillation, the fractions boiling between 92°C and 97°C at 4-5 mm. were redistilled. The final boiling point was 79.0°C/0.7 mm, n_D^{20} 1.4730. Yield: 107 g., 66% of theory.

2. N-iso-Propylacrylamide

This monomer had been prepared in connection with another project of this Laboratory. The required quantities of material were made available to this project.

3. N-n-Butylacrylamide

To a chilled solution of 337 g. (4.62 moles) of n-butylamine and of 500 g. (5 moles) of triethylamine in 1500 ml. of benzene was added a solution of 430 g. (4.75 moles) of acrylyl chloride in 500 ml. of benzene over a 4 hour period.

The salts were filtered off. The solvent was removed from the filtrate by distillation. The fraction with boiling range from 97°C/3 mm. to 120°C/4 mm. was preserved. This product solidified in the condenser, m.p. 13-14°C. Yield: 482 g., 62% of theory.

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The main fraction was fractionally distilled, 360.6 g. of product were recovered b.p. 102-104° C/1-2 mm., n_D^{20} 1.4670, m.p. (equilibrium, corrected) = 16.0° C.

4. N-iso-Butylacrylamide

See section IB 2 above.

The product was redistilled prior to use, b.p. 100-101.5° C/4-5 mm., n_D^{20} 1.4652.

5. N-tert.-Butylacrylamide

This monomer was available from a commercial source. The recrystallized sample used in this work was made available to us from another project.

6. N-tert.-Octylacrylamide

The commercially available monomer had to be crystallized repeatedly from textile spirits until a melting point of 58.5°-59° C (uncorrected) was observed. This material was considered suitable for future polymerization studies.

7. N,N-Dimethylacrylamide

After several attempts at synthesis that afforded only poor yields, the following, more adequate, procedure was evolved.

To a chilled solution of 460 g. (10.1 moles) of dimethylamine in 1000 ml. of benzene was added a solution 452.5 g. (5 moles) of acrylyl chloride in 1000 ml. of benzene over a 2 hour period.

The benzene solution was separated from the salts, the filtrate was fractionally distilled. The fractions, b.p. 77-79.5°C/18 mm., n_D^{20} 1.4722 to 1.4725 were collected as product. Yield: 232.9 g., 46.8% of theory.

8.   N,N-Diethylacrylamide

See section IB 2. The material was distilled prior to use. b.p. 116-117°C/46-47 mm.

9.   N-1,1-Dihydroperfluorobutylacrylamide

a.   Methyl Perfluorobutyrate

The preparation of this ester was carried out by the conventional method involving the treatment of perfluorobutyric acid and methanol with concentrated sulfuric acid.

b.   Perfluorobutyramide

Treatment of the above ester with an excess of ammonia afforded the amide in good yield.

c.   1,1-Dihydroperfluorobutylamine

The preparation of this amine involved the reduction of perfluorobutyramide with lithium aluminum hydride by the new method developed on a previous contract for compounds of this type (1). This reaction must now be considered hazardous.

d.   N-1,1-Dihydroperfluorobutylacrylamide

To a solution of 46 g. (0.23 moles) of 1,1-dihydroperfluorobutylamine, 30 g. (0.3 moles) of triethylamine, 0.1 g. of phenothiazine in 100 ml. of anhydrous ether was added 1 g. of powdered, dry barium chloride. The mixture was vigorously stirred in an ice-salt bath while a solution of 23 g. (0.255 moles) of acrylyl chloride in 50 ml. of anhydrous ether was slowly added. The solid was filtered off, the filtrate was distilled. The ether was evaporated off. The residue weighed 49 g., yield 89%. The solid was recrystallized from textile spirits.

10.   N-1,1-Dihydrotrifluoroethylacrylamide

The preparation of this compound followed the same lines as that of N-1,1-dihydroperfluorobutylacrylamide. As mentioned in the discussion section, the preparation of the amine was successful once and exploded violently when an attempt was made to repeat it. This reaction also can no longer be considered a safe one.

C.   Perfluoropropoxyethyl Acrylate

1.   Use of Silver Oxide

                In a 300 ml. three necked flask fitted with a stirrer,
Dry ¹ce condenser and addition funnel were placed 6 g. (0.05 moles) of
hydroxyethyl acrylate, 100 ml. of benzene, and 6 g. (0.025 moles) of silver
oxide. After 1 g. of silver nitrate had been added to this mixture, a solu-
tion of 14.5 g. (0.5 moles) of 1-iodoperfluoropropane diluted to 50 ml. with
benzene was added at room temperature. After one hour of rapid stirring and
no visible chemical change, the mixture was refluxed for one and one half
hours. No visible reaction took place. The addition of a few drops of water,
in case moisture was required for the reaction to proceed, brought about no
further changes and the reaction was abandoned.

2.   Use of Metallic Sodium

                In a set up as described in 1, above, 1.3 g. (0.5 moles)
of sodium was added to a solution of 150 ml. of benzene, 6 g. (0.05 moles) of
hydroxyethyl acrylate, and 14.5 g. (0.05 moles) of 1-iodoperfluoropropane.
¹he mixture was refluxed with rapid stirring for two hours. To the warm solu-
tion, 10 ml. of methanol was added to react with the sodium. A few grains of
phenothiazine as inhibitor were added and the solution was allowed to cool.
After 10 ml. of water had been added to the mixture, the organic layer was
drawn off and dried by shaking with sodium sulfate. The solvent was evaporated.
The residue was a tarry substance, which could not be distilled. The nature of
this polymer was not ascertained.

3.   Preparation of the Intermediate 2-Perfluoropropoxyethanol

                In a 500 ml. three necked flask equipped with stirrer,
condenser, and addition funnel, 200 ml. of ethylene glycol and 1.3 g. (0.05
moles) of sodium were rapidly stirred and gently warmed. After the sodium had
dissolved completely, 50 ml. of a benzene solution containing 15 g. (0.05
moles) of 1-iodopropane was added. The mixture was heated to reflux for two
hours. During this time the reflux temperature gradually rose from 33° to
65° C.

The mixture was divided into three fractions by distillation.

                Fraction I   42-77°C
                         II   62-98°C
                        III   192-196°C

Fractions I and II were combined, fraction III was discarded as ethylene glycol. The combined fractions I and II were redistilled through a short column. The following fractions were isolated:

Fraction A	33-44°C/758 mm.	2.5 g. C_3F_7I
B	55-70°C	7.0 g.
C	76-79°C	benzene

If fraction B is perfluorohexane, taking the recovered 1-iodoperfluoropropane into consideration, the yield was 98%.

D.   1-(1,1-Dihydroperfluorobutoxy)-3,3,3-trifluoro-2-propyl Acrylate

1.   1,1,1-Trifluoro-3-bromopropanone

A 5-1, 3 necked flask containing 500 ml. of concentrated sulfuric acid and fitted with an efficient condenser, a stirrer with a Teflon blade, and a gas inlet tube extending below the level of the acid, was cooled in an ice bath. Through the gas inlet tube, 194 g. (1.73 moles) of 1,1,1-trifluoropropanone was distilled into the acid.

Then an addition funnel holding 138 g. (1.73 moles) of bromine was substituted for the gas inlet tube, and the bromine was added over a two and one half hour period with vigorous stirring. Agitation was continued for an additional hour.

The sulfuric acid layer was then separated from the lower product layer. The acid layer was distilled and all material distilling up to 145°C was combined with the product layer. The product was fractionally distilled. The fraction boiling between 83 and 92°C was considered the product, weight 24.3 g. (The yield was 73%).

Two higher boiling fractions were also isolated. One, b.p. 105 to 107°C/atm. press. weighed 23.6 g.; the other, b.p. 55-78°/83 mm. weighed 4.6 g.

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. 2. 1-(1,1-Dihydroperfluorobutoxy) -3,3,3-trifluoropropanone

a. To 25 ml. of an aqueous solution containing 4 g. (0.1 moles) of sodium hydroxide in a 125 ml. Erlenmeyer flask fitted with a reflux condenser was added 20 g. (0.1 moles) of 1,1-dihydroperfluorobutanol. The resulting sodium salt was not completely soluble in this quantity of water at room temperature.

Over a one half hour period, 19.1 g. (0.1 moles) of 1,1,1-trifluoro-3-bromopropanone was added. As the addition proceeded, the salt went into solution and a two phase system gradually formed. Both layers were slightly reddish brown. The mixture was heated on a water bath for 2.5 hours. Then the layers were separated. The aqueous layer was extracted several times with ether, the ethereal solution was added to the organic layer, and the whole mixture dried with anhydrous sodium sulfate.

By repeated fractional distillation of the product solution the following fractions were separated:

Fraction No.	B.P. Range, $^{\circ}$C	Wt., g.	n_D^{20}
I	83.5-88	4.5	1.3018
II	88-91	9.3	1.3150
III	91	2.3	1.3255
Residue		3.2	

b. In a 300 ml. boiling flask fitted with addition funnel and reflux condenser, 10 g. (0.25 moles) of sodium hydroxide was suspended in 100 g. (0.50 moles) of 1,1-dihydroheptafluorobutanol. The mixture was warmed for approximately one half the reaction time while 47.9 g. (0.25 moles) of 1,1,1-trifluoro-3-bromopropanone was added over a 0.75 hours period; the mixture was refluxed for 4½ hours. The solid was filtered off. The filtrate was dried with calcium chloride.

Distillation of the dried liquid with some o-xylene as chaser, afforded the following fractions:

Fraction No.	B.P. Range, $^{\circ}C$	Wt., g.	n_D^{20}
O	80-89	3.8	
A	89-93	35.2	1.3320
B	93.5-98	35.7	1.3133
D	98-102	2.5	1.3318
E	102-137	2.2 (partially solid)	

Fractions A, B, and D were combined and washed repeatedly with 10% NaOH solution. The organic layer was separated, the aqueous layer was extracted with ether several times. The combined ether extract and organic layer were dried first over magnesium sulfate then over Drierite.

Fractional distillation of the material afforded two main fractions:

Fraction No.	B.P. Range, $^{\circ}C$	Wt., g.	n_D^{20}
A-2	93-96	16.0	1.3320
B-2	97	16.1	1.3133

The alkaline wash was neutralized with concentrated sulfuric acid and distilled. The product collected up to 100°C, $n_D^{27.5}$ 1.3396 (Fraction C-2) was preserved for possible future identification.

The identification work of these fractions is dealt with in the Discussion section.

II. Polymer Preparation

Three methods of copolymerization were utilized in connection with this project. These were suspension polymerizations in a stirred system, suspension polymerization in capped bottles which were shaken, and bulk polymerization.

The procedure for the stirred process may be outlined thus:

In a 1-1, three-neck flask, fitted with a "half moon" type stirrer, (usually made out of Teflon), a reflux condenser, and a thermometer-well holding a thermometer, was placed 400 ml. of distilled water whose viscosity had been adjusted by the addition of varying quantities of soluble starch.

The nominal solution of comonomers was prepared separately. Freshly reprecipitated dibenzoyl peroxide was dissolved in the comonomer solution just before this solution was to be added to the water medium.

The water substrate and catalyzed comonomer solution in the flask was stirred at 862 r.p.m. The assembled equipment was then immersed in an oil bath which had been heated to a temperature approximately 10°C above the temperature at which the polymerization was to be carried out.

Once the reaction became self-sustaining, the oil bath was removed until the thermometer in the flask indicated a drop in temperature. The approximate peak temperature was recorded.

After the reaction had subsided, the reaction mixture was heated to reflux for a short time. Then the excess monomer was steam distilled from the reaction mixture by attaching a Dean and Stark distillation receiver between the reaction flask and the reflux condenser. Usually, before 10 ml. of water had been distilled out, the free monomer in the receiver had reached a constant level.

The product was filtered through a silk bolting cloth and washed with boiling distilled water until the wash water was quite clear. The product was then air-dried overnight followed by a 24 hour drying period in an oven at 65°C.

In Table XXVII the pertinent data for a representative selection of these copolymerizations is given. For compositions of a given rubber, reference are made to Table I opposite each code number.

Column A, states the code number of the copolymer, 9000-1- and the compositions.

Column B, weight of starch, g., used in 400 ml. of water.

Column C, combined weight of monomers, g.

Column D, total weight of dibenzoyl peroxide used, t= 0.1 g., h= 0.05 g.

Column E, approximate peak temperature, $^{\circ}C$.

Column F, approximate time required to reach peak temperature, minutes.

Column G, percent yield of polymer.

TABLE XXVII

Data for the Preparation of Some Copolymers

A	B	C	D	E	F	G
10, EA-5AA	1	100	t	*	*	88.4
15-2, EA-5tBAA	0.5	100	t	87	30	90.6
15-3, EA-5tBAA	1	100	t	86	45	86.2
15-4, EA-5tBAA	1.5	100	t	85	35	88.5
17, EA-12tBAA	1	100	t	86.5	40	87.8
19, TFEA-1tBAA	1	100	t	85	56	84.8
21, TFEA-5tBAA	1	100	t	86	50	88.8
25-A, TFEA-1AN	1.25	100	t	77	150	92.5
25-B, TFEA-5AN	1.25	100	t	76	155	78.8
25-C, TFEA-10AN	1.25	100	t	75	160	70.0
29-21, TFEA-5iBAA	1.5	100	t	85	41	92.7
29-22, TFEA-10iBAA	1.5	100	t	87	32	90.8
31-26, TFEA-5MAA	1.5	50	t	85	48	84.4
31-27, TFEA-10MAA	1.5	50	t	84	37	68.8
33-34, TFEA-10BAA	1.5	50	t	82	52	91.8
33-35, TFEA-5BAA	1.5	50	t	82	52	90.2
35-38, TFEA-5iPAA	1.5	50	h	83	72	80.4
35-39, TFEA-10iPAA	1.5	50	h	84	45	80.8
41-42, TFEA-5DEAA	1.5	50	h	73.5 to 78	20**	37.8
41-43, TFEA-10DEAA	1.5	50	h	73.5 to 79	17**	36.0

* maintained at 80° C ± 5°C for 1 hour and 55 minutes.
** remained in the peak temperature range for 30 minutes.

A solution of polyvinyl alcohol could be substituted for starch in the aqueous substrate. The preparation of FBA-39.6 mole % AN is an example.

A solution of 44 g. of FBA, 6 g. of AN, and 0.005 g. of dibenzoyl per-oxide was copolymerized in suspension with 400 ml. of distilled water and 6 ml. of a 1% solution of Polyco 270A (American Monomer Corp.) at 80°C for 5½ hours with rapid stirring. On steam distillation, 21.8 g. of monomer was recovered. The polymer that was isolated weighed 24.6 g., an 88% yield if recovered mono-mer is taken into consideration.

As indicated in the discussion section, a number of copolymerizations were carried out by shaking comonomer solutions and an aqueous medium containing various catalysts on a reciprocal shaking machine.

The preparation of glass cells for bulk polymerization, was done as follows:

One side of each of two 3½" x 4" lantern slides was coated with a parting agent such as Solricin 535 (Baker Castor Oil Co.), four small pieces of glass, approximately 5 x 5 x 3 mm., were placed in the corners of one of the lantern slides, and the other slide was positioned over these four spacers so that the two coated glass slides would face each other and be separated by a distance of 3mm.

By use of spring clothclamps, this assembly could be handled further. A 1 inch parchment tape was soaked in aqueous glue and fastened around the edges of the glass layers much as lantern slides are taped. The cell was then allowed to dry slowly. Two adjacent holes were punched into the top of the tape to furnish a means to fill a cell with liquids.

The tightness of the seal could be tested by introducing a little ether into each cell and by observing whether the tape held. Then each cell had to be redried by gentle heating. Considerable practice was required before a reasonable number of cells could be prepared that were liquid-tight.

The solution of monomers and catalyst could be introduced through the holes previously punched into the tape. The assembled cell was heated in a

vertical position in a constant temperature oven.

One batch of trifluoroethyl polyacrylate was prepared accidentally, when the contents of a bottle of the uninhibited monomer polymerized at room temperature.

III.   Swell Tests on Elastomers

Milled but uncured elastomer samples were cut to approximately 40 x 10 x 1.5mm. The dimensions were determined with a slide caliper, however, the distortions of the final sample were so large, that these measurements were of dubious value.

Each sample, fitted with a wire loop, was weighed in air, then in distilled water and finally dried by evaporation. The samples were placed in jars of 70% isooctane-30% toluene by volume and kept at room temperature, $25^\circ C \pm 5^\circ C$ for fourteen days.

Each sample was then removed from the solvent, dipped several times into acetone and gently blotted between filter papers. Some material was thus transfered to the filter paper.

The blotted samples were weighed in air and in distilled water. From these data, volume and weight variations were computed.

In later tests, samples which had distorted badly in the course of the test, were placed in screen baskets prior to weighing. For computation purposes, these baskets were weighed in air and in distilled water prior to their use.

Raw elastomers were also tested by placing samples into screen baskets.

IV. Weight Changes With Time

Weighed samples of milled, but uncured, elastomers were placed on weighed aluminum dishes. After the initial weighings, all were placed in a constant temperature oven at $96^\circ \pm 3^\circ C$. After 15 minutes the dishes were removed from the oven, cooled, and weighed. This procedure was repeated at intervals until the rubbers had been subjected to the equivalent of 4 hours of heat treatment.

This procedure was also utilized in a second series of weight change vs. time experiments. In these cases, the time intervals were somewhat different.

V. Heat Resistance Test

Fresh weighed samples were placed in weighed aluminum dishes. The assembled samples were heated in the constant temperature oven at $148^\circ \pm 5^\circ C$ for 72 hours. After this period, the samples were cooled and weighed.

Then the samples were returned to the oven and treated at $204^\circ \pm 5^\circ C$ for 90 hours. After this second period, the samples were again cooled and re-weighed.

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APPENDIXES

I.   Conferences Attended

We had occasion to confer with Dr. Banus, director of research, H. Mustonen and other members of the technical staff of Metal Hydrides, Inc. at their facilities in Beverly, Mass.

It will b. recalled that an explosion took place while reducing a fluorinated amide with lithium aluminum hydride. The purpose of our visit to the manufacturer of the hydride was

    a)   an attempt to determine the causes of the explosion,
    b)   to ascertain whether alternative procedures were available,
and if not, whether this company would undertake the reductions for us under their program of "custom reductions."

With regard to this latter point, it was indicated to us that no reductions could be carried out at Metal Hydrides, Inc. that might represent a hazard to their facilities as well as a danger to the city of Beverly.

Although we discussed the background and details of our experience at great length, no definite cause for the explosion could be ascertained. It was pointed out that trouble might arise if aluminum hydride should form in the course of the reaction. This material is considered to be quite unstable. The manner of formation was highly conjectural. One suggestion was that the lithium moiety of the reducing agent abstracts a fluorine from the molecule, leaving aluminum hydride. We felt, however, that rupture of a C–F bond by the reducing agent would be extremely unlikely. Our reasoning is based on the bond strengths of C-F, C-H, and C-Cl. The C-F is thermally the most stable of the three, while the C-Cl bond is the least stable. Admittedly, it is not necessarily valid that thermal stability data may be used to interpret data involving the use of various reagents. Yet, with all due caution, we may reason that since the stability of the C-Cl bond to lithium aluminum hydride is well known, the C-F bond will be even more stable rather than less stable. Hence the probability of forming the thermally unstable aluminum hydride is small.

The reductions of polyfunctional fluoro compounds were believed to be troublesome (21). The recommendation was made to follow the procedure of Smith and Reed prior to a run. This would involve treating a very small amount of $LiAlH_4$ with the material to be reduced in ether solution. The solvent should then be evaporated and the residue heated strongly on a hot plate to determine

the stability of this intermediate. It was suggested that even this test should be carried out behind a barricade.

As to alternative methods of producing these amines from the related amides, the possibility of utilizing potassium borohydride-lithium chloride mixtures was discussed. At this point, however, it is the feeling of this Laboratory that the use of these new, unconventional reagents can only be used for preliminary testing on a micro scale with adequate safeguards for personnel and property.

II. Papers Prepared

The preparation of silver perfluorobutyrate has been submitted to "Organic Syntheses" for consideration.

A report on the hazards of lithium aluminum hydride reductions of fluorinated amides has been submitted to Chemical and Engineering News and was published in the Spring of 1955. (22)